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Journal of METALS

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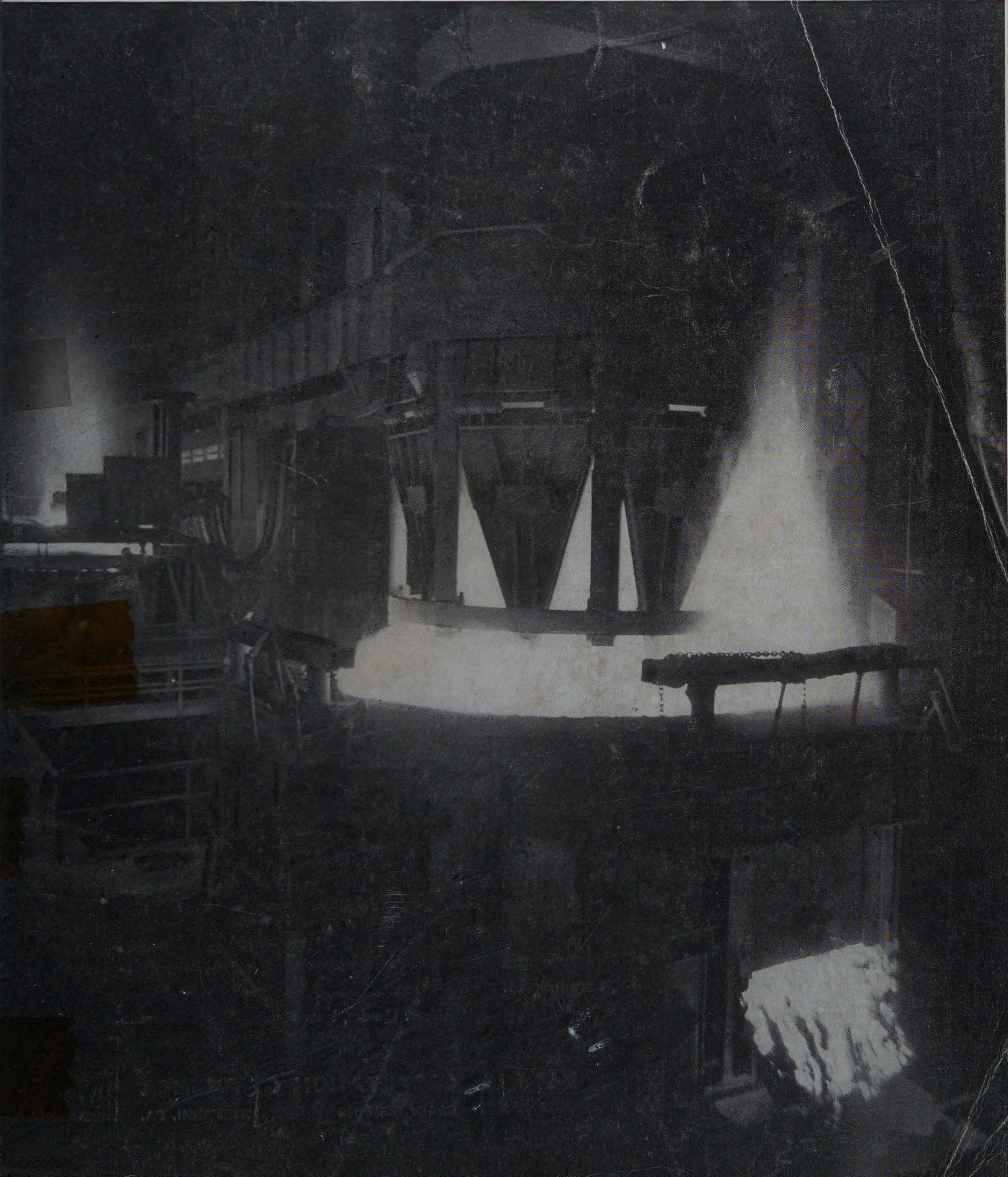

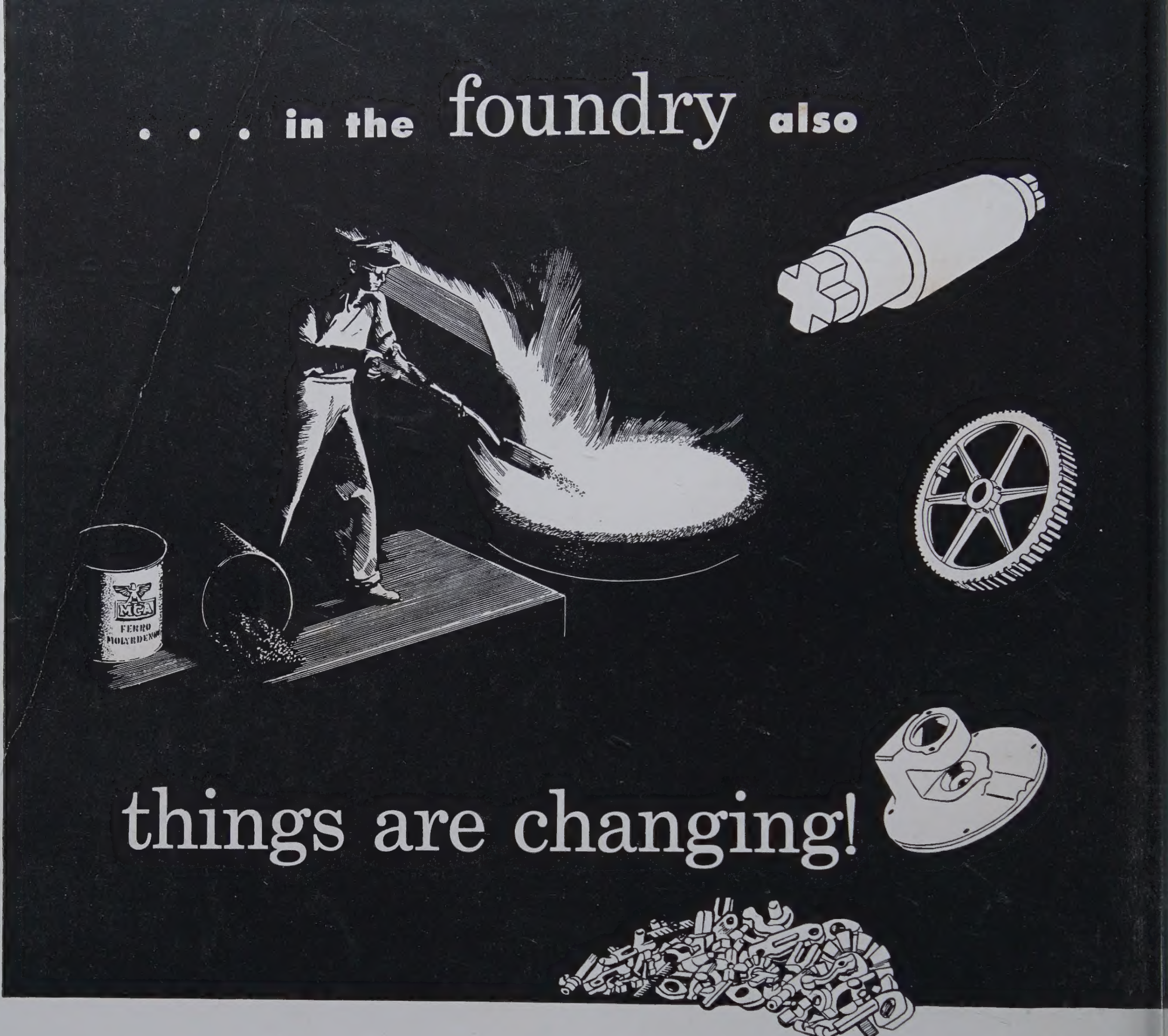

Progress means change, in the foundry as elsewhere. Competition sets the pace. Many light and heavy castings made for machine parts and various other uses, now have to compete with different methods of manufacture. Skills, judgment, and readiness to take advantage of new knowledge are demanded at such a time. A foundryman who is aware of the challenge needs to be well acquainted with the benefits of Molybdenum, Tungsten, and Boron in making better, stronger cast irons and steels.

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IN THIS ISSUE

VOL. I, NO. 11 NOVEMBER 1949

COVER

First and exclusive photo of Allegheny-Ludlum's new electric melt shop at Brackenridge, designed primarily for carbon and silicon steels. Shown here are two Swindell top-charge 70-ton units; two 60-ton units are being installed. The 70-ton furnaces are pushed hard with plenty of power, some 16,000 kva—even larger power imputs are planned. Average tap is 80 tons and average time tap-to-tap is 5 hr 28 min, although a 3 hr 15 min time has often been achieved.

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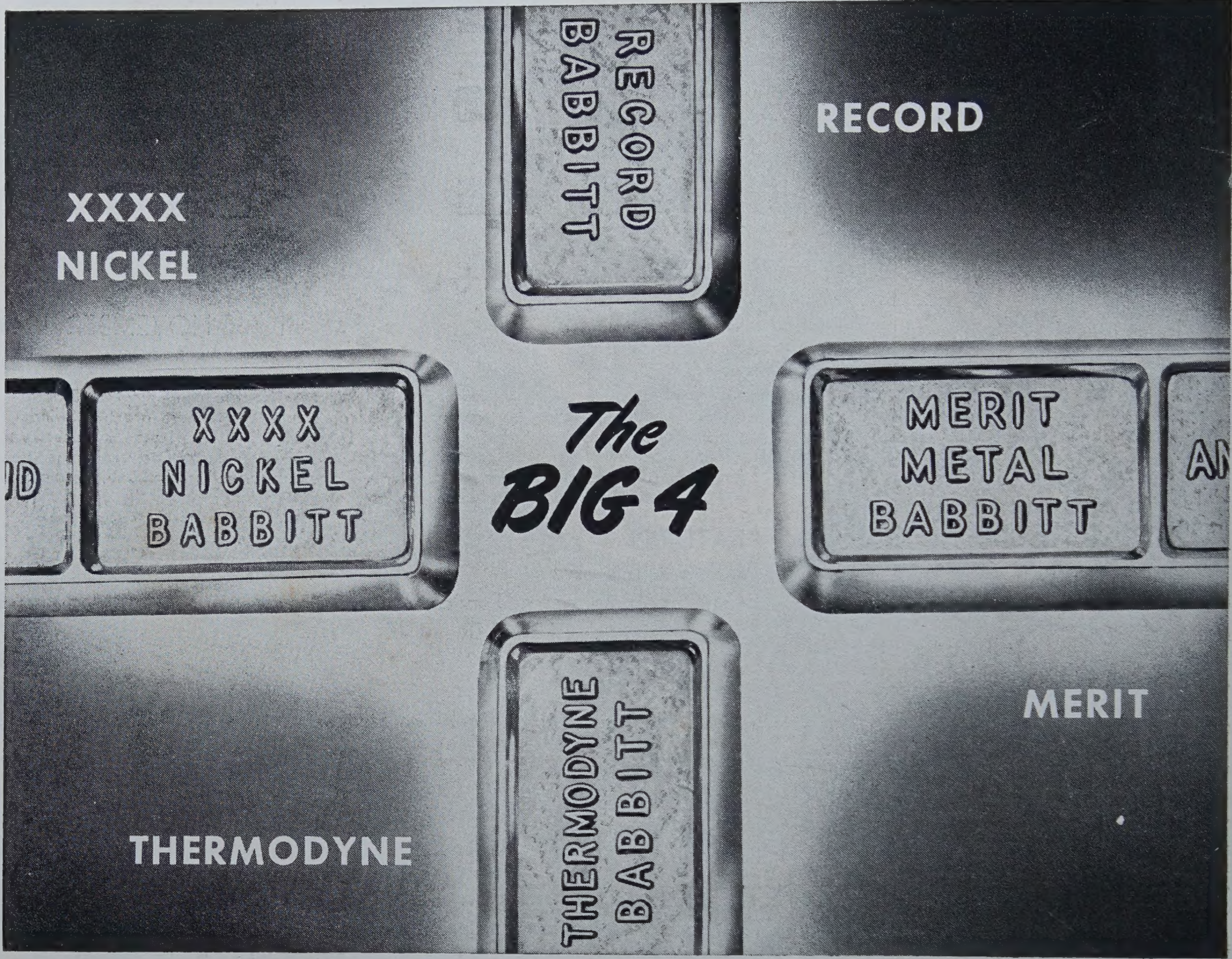

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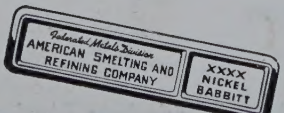

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Authors In This Issue

A. B. Wilder

V. W. Cooke

A. Levy

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H. Kenworthy

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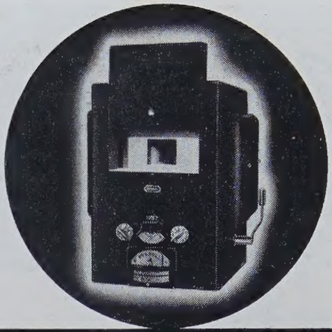

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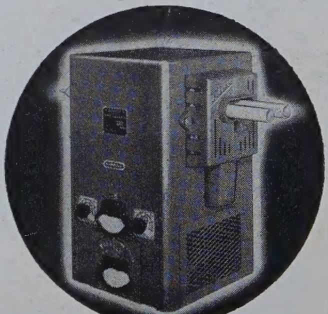

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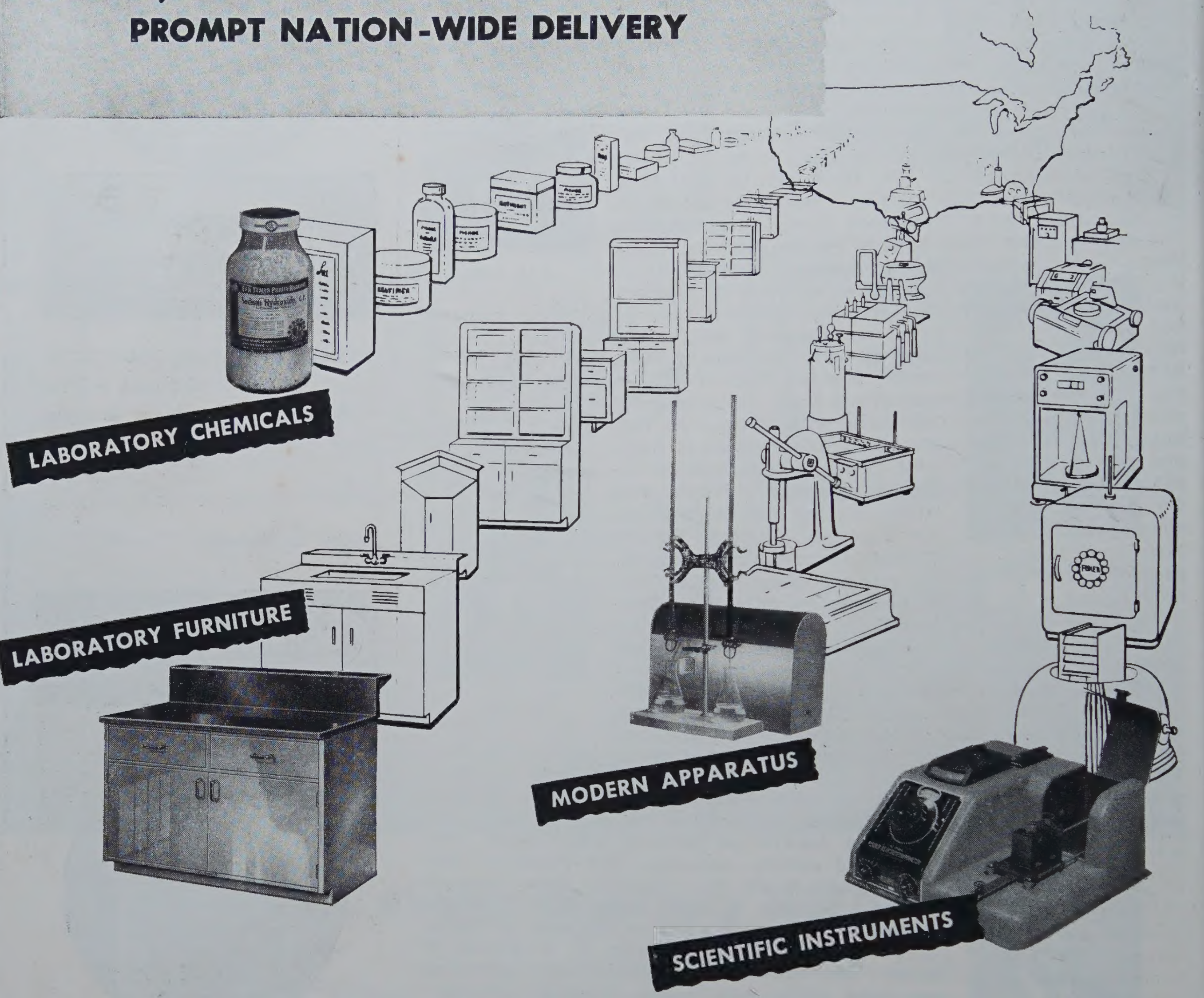

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mock and washing dishes is quite to his liking. . . . **G. E. Sims** (p. 814): born in Chicago, attended R. T. Crane Technical high school and University of Illinois and University of Utah, receiving degrees of B.S. in Ch. Eng. and M.S. in Met. He is a member of AIME and lives in Columbus, Ohio. Was associated with Anaconda Copper Mining Co., Aluminum Co. of America and was Electrometallurgist and Associate Metallurgist for U. S. Bureau of Mines, Asst. Director of Research for American Steel Foundries; Supervisor and now Asst. Director of Battelle Memorial Inst. Mr. Sim's chief recreations are fishing and golfing. . . . **F. W. Boulger** (p. 814): born in Minneapolis, attended Cretin high school, holds a Metallurgical Engineer's degree from Univ. of Minnesota and M.Sc. degree from Ohio State Univ. He is a member of AIME and lives in Columbus, Ohio. Was with the Republic Steel Corp. and is now a supervising metallurgist in steel processing research at Battelle Memorial Inst. During 1936 Mr. Boulger was a Battelle Fellow in Metallurgy at Ohio State Univ. He is a member also of the ASM, AFS, technical societies and Sigma Xi, honorary scientific society. . . . **N. J. Grant** (p. 898): born in South River, N. J., attended South River high school and graduated from Carnegie Tech with S.B. degree and D.Sc. degree from Mass. Inst. Tech. He is a member of AIME and lives in Winchester, Mass. Has previously presented AIME papers on Sulfur Equilib. Between Liquid Slag and Metal, and Introduction to Gases in Steel. His recreations are fishing and gardening. . . . **R. G. Knickerbocker** (p. 785): born in Napoleon, Ohio, attended Logansport, Ind. high school and graduated from the Missouri School of Mines and Metallurgy with degree of B.Sc. and Met. Eng. Now lives in Rolla, Mo. Is a member of AIME. Now Chief of Metallurgical Branch of Bureau of Mines at Rolla, Mo. . . . **C. H. Gorski** (p. 785): born in Brooklyn, attended Brooklyn Technical high school and graduated from Pratt Inst. and New York University with degrees of B.Ch.E, and M.Ch.E. He is a member of AIME and resides in Rolla, Mo. At present with Bureau of Mines, Rolla, Mo. as Metallurgist.

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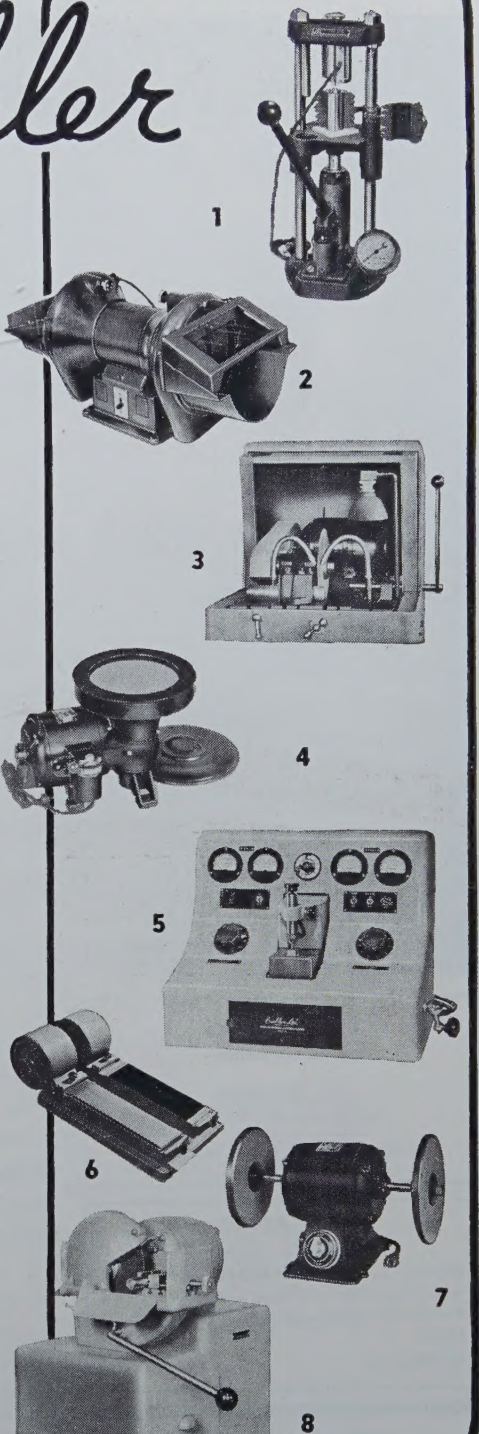

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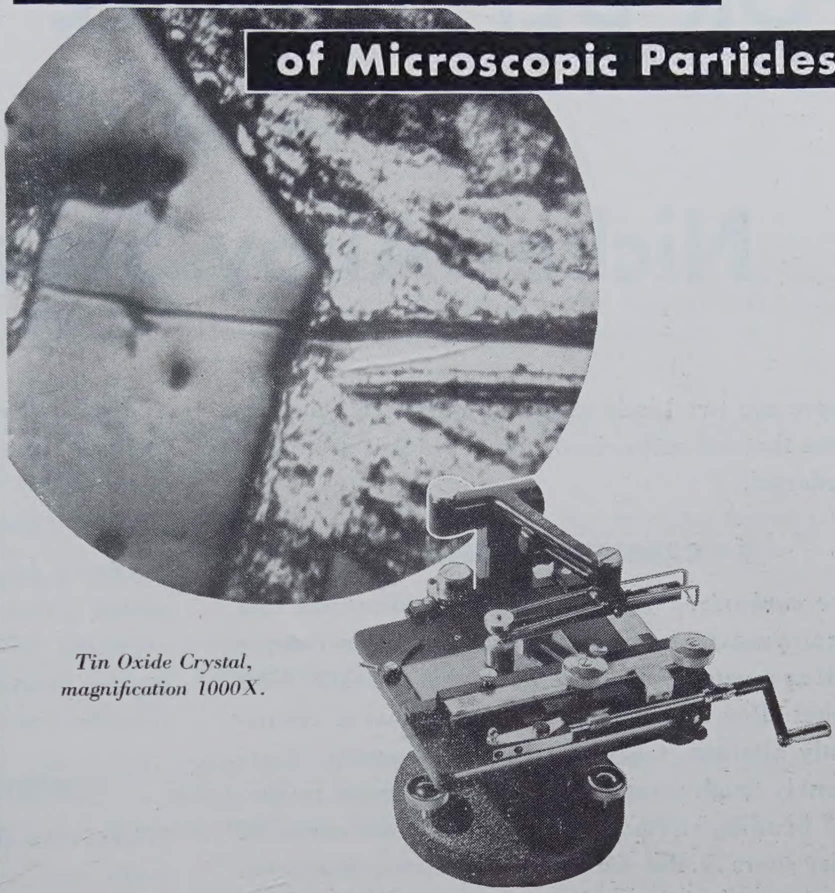

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NEW YORK 5, N. Y.

Journal of Metals REPORTER

* Greater recovery of manganese from openhearth flush-off and tap slags is possible by several plans proposed by Vignos (p. 20.) In killed steels greater use of silicon can improve manganese recovery and several plants are getting better recovery by using ladle additions.

* Bessemer converter operation, along with investment costs, blowing time, quality and oxidation are described by Wilder (p. 22).

* Three new procedures for solid-phase bonding of aluminum alloys to various steels are described by Cooke and Levy (p. 23). Bond strengths are very high and the new processes may open up a new series of composite metals.

* Melting cycles in an electric furnace shop have been reduced by 26 pct and man-hours per melted ton reduced by 19 pct by means of proper materials handling. F. O. Lemmon tells all about it on p. 35.

* Algoma steel has proved two new high-grade ore bodies from which 12 million tons can be mined by open-pit methods before going to underground mining. Known as Siderite Hill, the new discovery is 3 miles west of Algoma's Helen mine and 100 miles north of Sault Ste. Marie.

* A new dolomite brick involving some radically new practices in refractory manufacture will soon be announced by a prominent producer. Laboratory and service tests so far indicate startling performance records.

* The dial telephone is going through another design change to make it more functional. In about a year a new instrument will appear about half the weight of the present one and will permit dialing from about any position.

* For the first time, Eastern Stainless, Baltimore, is melting its own steel. They are using a battery of Ajax high-frequency furnaces, and for the most part home scrap.

* The largest continuous casting unit in the world, a Rossi machine, is being erected for Imperial Chemical Industries in South Wales and will go into operation in January. Aluminum alloys will be continuously cast in 20-in. rounds and in slabs measuring 10 x 48 in.

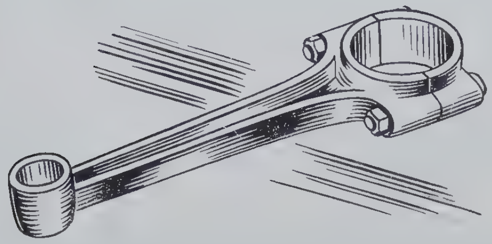
* Scovill Mfg. Co. will soon celebrate its new expansion in facilities. One feature will be its second continuous casting machine which has cast many thousands of tons of brass in sizes up to 12 in. diam and 4 x 28 in., the latter automatically cut in 16-ft lengths.

* Titanium tetrachloride and titanium oxide can be produced from rutile by smelting with pyrite and coke, and then processing the titanium matte (p. 791). Ultimate titanium recoveries of over 90 pct are obtained.

* A new dithionate process for treating oxidized zinc ores or low-grade zinc concentrates is described on p. 795.

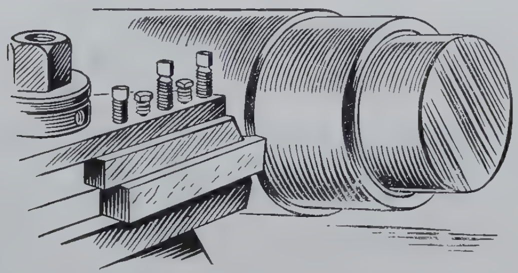
* A new type of indicator for studying the relative deoxidizing powers of elements used in the deoxidizing of steel, as well as results obtained, are described on p. 814.

how VANADIUM improves—



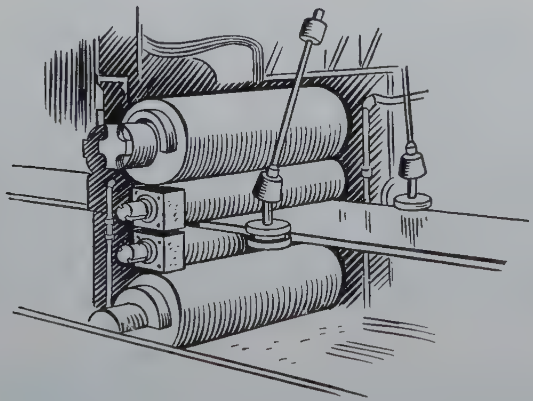
Engineering Steels . . .

Vanadium steels are tough because of their uniformly fine grain size. They are especially suitable for parts subjected to high dynamic stress. Vanadium-bearing steels also show exceptional resistance to abrasion and fatigue. Parts can be readily cast, rolled, or forged.



Tool Steels . . .

Nearly all fine tool steels contain vanadium. In the carbon-vanadium grades, this alloy helps control hardenability and improves cutting qualities. Vanadium carbides promote fine grain size and high wear resistance in all tool steels. High-speed steels depend on vanadium for a large measure of their high-temperature hardness.



Cast Iron . . .

In iron castings, such as those used for rolls in steel reduction mills, vanadium is an essential alloy. When added in amounts of 0.10 to 0.15 per cent, vanadium produces a marked increase in the strength of iron. Vanadium also helps produce castings which are remarkably free from growth and distortion and are suitable for service at moderately high temperatures.

Let our metallurgists show you how you can produce stronger, more uniform steel or iron by using vanadium. They will also gladly give you on-the-job technical assistance in the use of any other ELECTROMET ferro-alloy or alloying metal.

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The Steelworkers Say . . . .

A TAPE RECORDED INTERVIEW

ED. NOTE: A sampling of steel plants were visited and USA-CIO pickets were selected entirely at random for interviewing. The dates were Oct. 31 and Nov. 1, and the Bethlehem agreement had buoyed up hopes for industrywide settlement on the same generous basis. All men interviewed insisted on anonymity, not because of any particular fear but just to be on the safe side. Each man was interviewed separately, out of hearing of his fellow pickets. In general, the pickets were surprisingly articulate and well informed. Even though other settlements may be announced prior to publication, these interviews are presented to show what the average worker thinks of pensions and social services, and why.

No. 1

Q: What do you do in this plant?
A: Roller, skin pass roller. [About 45 yr of age.]
Q: What's the plant?
A: Why, it's J. & L.: it's the Otis Works.
Q: How long do you think this plant will be struck?
A: Well, that's something I wouldn't know—a week more, maybe!
Q: Really!
A: Yeah.
Q: What do you think of the Bethlehem settlement?
A: A good deal . . . we'll get that or better here . . . from what I get in the papers it looks like what we've been fighting for.
Q: Well, how about the 2½¢ per hr worker contribution for welfare; won't that reduce take-home pay?
A: I'd rather not say anything about that . . . anything Mr. Murray O.K.'s is O.K. with me.
Q: Don't you think the worker should contribute something to a pension system?
A: It doesn't make a bit of difference. They wouldn't be giving us anything if they paid it all. They know that . . . we'll be contributing it all even if they pay it all . . . it's compulsory saving, that's all.
Q: If you contribute nothing maybe you won't have much control over administration of the pension fund!
A: Oh! Our Union will take care of that . . . don't worry about that.
Q: How much retirement per month would 6¢ an hr. give?
A: Well, that all depends on the time element. Look at the number of men working and figure it out for yourself . . . A man could get $300 a month and they wouldn't be out a penny.
Q: Should the government have stepped in and forcibly settled the strike immediately?
A: Well, maybe not immediately . . . but if it isn't settled soon, it'd be no more than proper for them to do so . . . government pays pensions to their own workers . . . we're part of the government . . . we only ask what the government does for their own workers . . . nothing unreasonable.
Q: Does the CIO have a retirement plan?
A: That I don't know. Couldn't answer that question . . . fit and proper that they do so.
Q: Do you think everyone in the country should have a pension system?
A: That's right. It shouldn't be employer controlled . . . but government controlled. The big shots stymied Social Security . . . now we're throwing it back in the government's lap . . . I don't even know whether this company will be here when I retire . . . I'd rather see it Social Security.
Q: Would you rather have a raise now than a pension system?
A: No sir . . . I'd sooner have a pension than anything in the world—not a million bucks—don't misunderstand me! Maybe I have a personal reason too . . . my old man is over 65 and is hardly able to work. What will he do, walk out . . . no one would give a damn.
Q: Well, then maybe it's Mr. Murray who's in an ivory tower!
A: He's winning, ain't he . . . anything he does is O.K. by me.

No. 2

Q: This is the Otis Works, J. & L., eh!
A: That's right.
Q: What's your job here?
A: Run a crane . . . in the warehouse. [About 50 yr of age.]
Q: What does your wife think of the strike?
A: She wants me to go to work . . . and soon!
Q: Do you think a retirement plan would work better if the worker paid some of the cost?
A: Well, I don't know . . . I was just as well satisfied as before. After 65 yr persons ain't no good . . . somebody has to take care of them.
Q: How much retirement pay per month would 6¢ an hr give?
A: I don't even know . . . I'm not much . . . I just do my duty and what they ordered me out for . . . they figure $125 a month at least.
Q: Do you think the grocer and the plumber, and everyone, should have a pension?
A: Well, I don't know about farmers . . . they're on pensions all the time . . . they don't go on with the whistle or go off with the whistle.
Q: What did you think of the Bethlehem agreement?
A: I don't know . . . I didn't read much about it . . . the fellows around here are pretty happy about it.
Q: How about the 2½¢ an hr that the worker contributes—that reduces your take-home pay.
A: I don't like that . . . 2½¢ an hr and a 40 hr week —that makes $1 a week . . . but the fellows here say we would get hospital insurance for all the family . . . insurance . . . benefits . . . it doesn't look so bad . . . maybe later on we can make it better.
Q: How about a raise now instead of a pension?
A: Well, I don't know . . . get a raise and everything goes up . . . pensions are better.

No. 3

Q: What do you do here?
A: Normalizer . . . I'm a normalizer operator.
Q: What is this plant?
A: There's the sign . . . Republic's 98-in strip mill—biggest in the world, so it says!
Q: How long will the strike at this plant last?
A: Frankly I don't know . . . it's pretty critical . . . not long . . . it looks like they're beginning to fold.
Q: What has your wife said about the strike?
A: She's never told me . . . she feels whatever I do is all right.
Q: Do you think a retirement plan would be better if the worker paid some?
A: What would I think . . . I'm an officer of the union . . . why pay 5¢ or 4¢ more . . . those big boys, what

the hell are they . . . they don't pay anything . . . that's the way I feel.

Q: How much retirement per month would 6¢ an hr give?

A: Well, to be truthful I don't know . . . our leaders say the government says it's all right. We pay our dues into the organization and they have a research department that figures all that out . . . I'm 42 yr old and by the time I'm 65 I have socked away into the fund maybe $5000 for my own pension.

Q: Should the government have forcibly settled the strike immediately?

A: I don't believe in beating anyone's head in . . . it's tough all the way around . . . government shouldn't come in . . . but if two sides are at loggerheads only the government is big enough to come in . . . we don't need it yet.

Q: Some of the companies say they can't afford this pension payment!

A: I'll agree to anything the Union officers agree to . . . they're not out to put anyone out of business.

Q: How about a raise now rather than fighting out the pension business?

A: If you got a raise you'd just get more inflation. Look at those old men living in shacks over around Lakeside Avenue . . . they produced at one time . . . maybe some of them are bums but the average person is steady . . . They haven't made out very well!

Q: This is quite a gentlemanly strike, isn't it?

A: Sure, that's the best way . . . then there's no hard feelings when it's all over. The company let us have this shanty and ran electricity in for us . . . we even have television . . . see the aerial? If the company wants anything they ask us—they don't tell us. There's a pile of coal down there on fire . . . We let some men in today to put it out . . . I bet they'll be on it a month. They piled up a lot of coal to try to outsmart Lewis.

Q: Do you expect any trouble?

A: Hell no. We run the communists off the place . . . that's the reason I asked you so many questions . . . we got orders to throw anybody off that doesn't look right. Phil Murray runs a democratic Union. Why, downtown . . . in the meeting . . . everyone gets a chance to speak . . . if I raised my hand I got the floor from him . . . several times I told some guy to sit down when he kept jumping up to run off at the mouth.

Q: Do you think everyone in the country should have a pension?

A: I'll tell you, it's just like this . . . I remember when John Carey [Sec'y CIO] said that Social Security would have to expand and that the politicians were all teamed up to keep it small . . . that's what we put Congress in last year for. It has to expand . . . why a friend of mine has parents who just came from Germany and they get a pension . . . Germany had pensions even before the first war.

No. 4

Q: What's your job?

A: Second helper. I work in the openhearth.

Q: What's this plant?

A: Republic.

Q: Does it have some name, some company name?

A: Well, this was the old Corrigan Works.

Q: How long do you think the strike will last at this plant?

A: Oh, a week or so yet . . . I figure. Some of these fellows can't take it as well as I can . . . they have kids and they'll be broke in another week . . . some of them are around borrowing now.

Q: What does your wife think of the strike?

A: I'm single.

Q: This is the most friendly strike I ever saw!

A: I'll say . . . nobody's mad at anyone. It's just one big happy family . . . the cops bring us out coffee . . . they let us have juice for the radio there . . . we pick up telephone calls in the office there.

Q: About the only thing left would be to have Mr. White come down and entertain you with a mouth-organ solo.

A: Yeah . . . Well, he'd probably come nearer to it than . . .

Q: Do you think your company will follow the Bethlehem pattern?

A: All those steel companies are competitive . . . they can't let one do something better . . . I don't see how they can give us a worse settlement . . . I bet it's better!

Q: Would you rather have had a raise than settle for a pension system?

A: I don't think we'll get any raises for a long time . . . hell, my granddad got a pension in the old country.

No. 5

Q: What's your job?

A: I'm a roller—cold roller.

Q: What's this plant . . . American Steel & Wire Co?

A: That's right, Cuyahoga Works.

Q: And how long do you think the strike will last at this plant?

A: Oh, all the men in there think we'll be back in another week . . . the papers say a lot of companies will be signing soon.

Q: What does your wife think of it?

A: Well, you know women . . . she wants me back on a payroll.

Q: Do you think the worker would have better control over a pension plan if he paid some money?

A: Our main idea is to get it started in the first place then work on it from there on.

Q: How much retirement pay per month would the 6¢ an hr give?

A: I don't think it would give you over $50-$60 a month.

Q: That's the closest anyone has come to the proper figure. Do you think the government should have come in and settled the differences before the strike was called?

A: I think so, yeah. If they couldn't settle it by themselves the government might as well step in.

Q: Do CIO officials contribute to their own pensions?

A: I wouldn't know that either. [Ed. They don't, according to the best information available.]

Q: Should everyone in the country be on a pension system?

A: Everyone at 65 should have some kind of pension.

Q: The same size pension?

A: Well, maybe not . . . they should all have a minimum anyhow.

Q: Would you like to have your Local settle on the same basis as the Bethlehem agreement?

A: I'd go for that, yes. Eventually it'll come to that anyhow.

Q: Would you rather have a raise than set up a pension system?

A: I'm for the pension . . . I've got 22 yr service . . . some of the young kids are hot for a raise but later on they'll change their minds . . . a pension's better . . . although $100 a month ain't so much, but it'll help.

Q: Mr. Murray said that steel executives are up in an ivory tower and wouldn't come down to discuss the pension problem. Do you think that is true?

A: I wouldn't know.

Q: How about the offer by Colvin, president of Crucible, to debate the problem. Murray sidestepped that one.

A: Where was that . . . I didn't see anything about it.

Q: In Pittsburgh . . . a radio station offered to give radio time.

A: I didn't see anything about it . . . if it's true it doesn't sound so good.

No. 6

Q: What's the name of this plant?

A: Edgar Thompson plant.

Q: What's the company?

A: Carnegie-Illinois.

Q: What do you do in the plant?

A: Blast furnaces—I work on a blast furnace.
Q: How long do you think the strike will last in this plant?
A: That's a hard question to answer . . . until this thing boils down a little more. There's difficulty on both sides.
Q: What's the strike about?
A: Pensions . . . old age pensions.
Q: Are the steel companies willing to pay for old age pensions?
A: Well, the steel companies do pay an old age pension but it's not enough to live on.
Q: Do you think the pension you're asking for is enough to live on?
A: Maybe not very well . . . but it's a lot more than we're getting now.
Q: What do you think of the Bethlehem agreement?
A: That's what we're after!
Q: A lot of workers seem to think higher Social Security would be better than company pensions.
A: That's right . . . They both should be higher.
Q: Most of the companies say prices of steel will have to up to take care of pension costs.
A: Don't you believe it . . . I don't see why . . . they're making lots of money.
Q: Well, what if it is true?
A: That's not our problem . . . that's their problem.
Q: How about everyone . . . should they get a pension and insurance?
A: I guess so . . . that seems right . . . somebody has to take care of people.
Q: Well, don't you think that might lead us to Socialism?
A: I wouldn't know about that . . . the government should take care of people.

No. 7

Q: What's the name of this plant?
A: Jones & Laughlin Steel Corp. Southside Works.
Q: What do you do in the plant?
A: Maintenance welder.
Q: The other men over there mentioned they were not striking for pensions now but for 25 yr from now.
A: I'm not so much interested in 25 yr from now . . . it's what we want now.
Q: For instance, if you have a pension in the steel mill then the plumber and the groceryman should come in for old age pension . . . Do you think that would be proper, too?
A: I think everyone should share equally.
Q: Do you think you should share equally with the sweeper in the plant?
A: Well, not equally . . . I mean everyone should share the costs for pensions.
Q: Do you think 6¢ an hr up to 65 would cover old age pension?
A: I think that would cover it . . .
Q: Some of the steel companies insist that they are absolutely unable to pay. Do you think that's true.
A: No, I don't think that's true . . . I think they can all well afford it.
Q: Without raising the prices of steel?
A: Yes . . . judging by the profits they're making and the statements they make in the magazines, they're making enough to pay for it.
Q: If everybody goes on pensions pretty soon everybody will be paying for the other man's pensions!
A: They should raise the Social Security.
Q: Do you think everyone should be on a pension system?
A: Yes, I do!
Q: Even if it raises prices on everything?
A: I don't see why prices have to go up—it'll just be a form of forced savings. For instance, the barber here, do you get Social Security? Barber—"No, if I get sick, I got nobody to pay for it. I get no benefits for anything." [Ed. Note: This interview was taking place in a small barber shop near the picket lines.]
Q: If the Social Security were higher you wouldn't have to get a pension system out of the steel companies.
A: Yes, indeed . . . it would be sort of an accessory . . . of course we would get the steel pension too.
Q: Do you think everyone should have the same pension?
A: Well . . . maybe not the same . . . there should be some differences . . . the barber shouldn't get as much as a fellow in the mill . . . he has his own business . . . he's his own boss.

No guns, no clubs, no goons, but television, radio and coffee on the double-quick. "Just like one big happy family."

No. 8

Q: Do you work in this plant?
A: Yes . . . I'm a maintenance man.
Q: What's the name of this plant?
A: Oliver Iron and Steel, Pittsburgh.
Q: Do you think 6¢ an hr would give a pension the strikers are asking for of $100 a month?
A: Yes.
Q: Do you think that's enough?
A: Well, it's not enough . . . but I think that will be enough for the time being.
Q: Do you think the steel companies can pay that?
A: Maybe not the fabricators, but I think the large steel companies can.
Q: In general, do you think the workmen should contribute anything at all to a pension?
A: I think the steel companies should go along with the Union right now. I think later on the companies should take a certain percentage out of a man's earnings toward that pension.
Q: Lots of times it is thought when a worker doesn't contribute to the plan he has no control over the plan and may be discharged before he is 65.
A: The companies couldn't do it . . . the Union would step in.
Q: What did you think of the Bethlehem settlement?
A: It looked like the jackpot to me . . . it's what we want.
Q: The worker under that agreement contributes 2½¢ an hr . . . his take-home pay drops somewhat!
A: That isn't very much . . . Look what he gets for it . . . it's O.K. by me.

It's Everyone's Business

NOV. 2—Like an old-fashioned wrestling match, industrial conflict has become rather an unspectacular affair of powerful contestants locked in excruciating but static embrace. There's a twitch here and a grunt there, with bored onlookers patiently awaiting the violent flurry of the final fall. Such a formalized affair rarely rates the front page. Early in the month the epic conflict in Yankee Stadium and Ebbets Field captured the headlines and later in the month there was a certain fascinated attention accorded the military as they celebrated the second birthday of unification with a noisy civil war.

Elsewhere in Washington, the report of the Joint Congressional Committee on Atomic Energy relative to Mr. Lilienthal's "incredible mismanagement" was finding it difficult to see the light of day. Mr. Hickenlooper entirely failed to substantiate his charges and hearings long ago ceased for lack of witnesses. Hickenlooper is the current Washington word for fiasco, which must cause him great unhappiness, as the original intention was to so impress the folks back home in Iowa as to assure re-election in November 1950.

Congress, with adjournment at long last in prospect, hastily hacked through a log jam of unfinished business and was barely able to give more than passing attention to the swan song—with its strains of foreboding—of Dr. Edwin Nourse, President Truman's chief economic adviser. Dr. Nourse foresees possible economic ruin and he laid the blame for his apprehensions on high Government spending, the inevitability of more inflation and the preoccupation of management and labor with their own security.

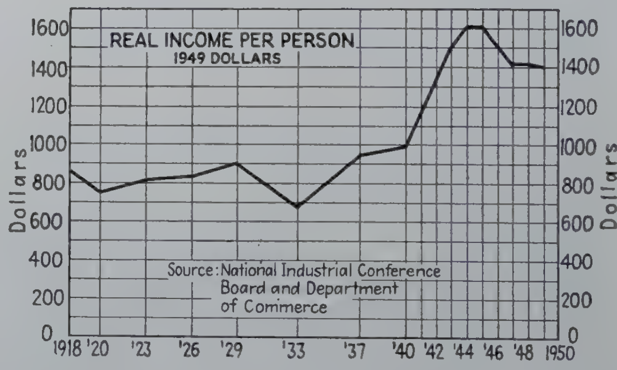
For the third time since the war the economy is being subjected to adverse events and developments of major magnitude. In 1945-46 the index of industrial production fell from 236 to 152, and in 1948 the index fell from 195 to a low of 162 in July 1949. In August there was a sharp recovery of 7 points and in September a few more points were added, but a chilling combination of blows in October pointed the index toward a new postwar low.

Indeed, the prospect of this decline has been enough to panic not only Dr. Nourse but quite a few other commentators. The prediction is that if current industrial strikes were not settled—and soon—the economy would slither into a quagmire of disaster. Many of these same commentators had been advocating a return to the bargaining table, but seem loath to accept the work stoppages that such a return entails. If the economy cannot stand these struggles for power it is indeed balanced on a thin edge, and the desire of many for government intervention to avoid such stoppages is symptomatic of the mental acceptance of the corporate-state philosophy.

It is true that the struggle for power between labor and management may have approached a particularly destructive stage. Furthermore, the basic position of the economy is undermined by very high taxes, the prospect of further levies for social insurance costs and disturbing dependence on unsound inflationary expenditure.

None the less, there is an underlying moderate tone of optimism among business men, civil servants and economists of various schools and connections. The war and postwar periods resulted in a buoyancy in investment that will not be lost for at least a few years yet. Financial reserves of individuals are still very high and are protected by social and private insurance and pensions. Large government expenditures serve to maintain both consumption and investment. Easy money is a pervasive stimulant. The economy contains no large area of over-extension or over-expansion to initiate a sizable collapse. And the increase in the population, which is far greater and more persistent than any estimates suggested, is another broad expansionary force.

Real income per person (see table) is now $1405 a year, which is almost double the level reached at the peak of the boom immediately following the first war and is 56 pct above 1929, 108 pct above 1933 and 41 pct above 1940. This 1949 figures indicates a standard of living of unprecedented abundance, and this has been realized despite the fact that nearly all segments of the community have been working considerably under the level of efficiency permitted by existing skills and equipment.



Source: National Industrial Conference Board and Department of Commerce

On the labor-management front, a major railroad strike was settled, the steel impasse began to crack but immovable mine owners continue to face immovable miners. Mr. Lewis, just a little disturbed by growing "return to work" sentiment among his miners, threw out a trial balloon to rally the AFL in joining his union in financial aid to the steel workers who, he trumpets, are under "vast and barbaric attack . . . to decimate all unions." But things never got desperate enough for such old enemies as Green, Murray and Lewis to fraternize in a common war chest.

To many a Pittsburgh steel man it appeared as if first young Ford and then, later, Bethlehem, sold the bridge. Bethlehem, however, was already deeply committed to pensions and the Ford company's willingness to discuss pensions is not new. Ford concluded that non-contributory pensions were bound to come, conceded the principle and concentrated on striking the best bargain possible. The scheme goes into effect next March and when pensions begin in April, car owners as well as coal users will begin to pay the price of old-age security. Steel users also will pay a price yet undetermined. Steel's opposition to non-contributory pensions was based on its shrewd suspicion that the size of pension that could be paid for by 6¢ an hr would not satisfy the steel workers for long, if at all.

Despite a series of relatively generous pension offers by steel companies, Mr. Murray was driven to an intransigence usually associated with Mr. Lewis. On Mr. Murray's left the fellow-travelers waited to exploit any failure and on his right Mr. Reuther already had a spectacular victory to his credit. The industry's united front seemed so monolithic and sentiment for a reexamination by the Steel Board of its recommendations was growing so fast that Mr. Murray approached the Cleveland CIO convention more in the role of a martyr rather than a victor. Bethlehem's capitulation on the opening day of the convention, however, was victory indeed, with a heady promise of pattern for the entire industry.

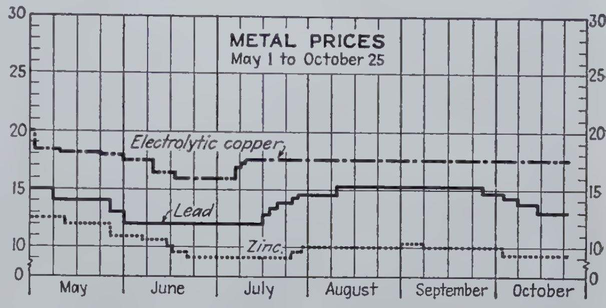
Despite newspaper articles offering dire predictions of industrial disaster because of the coal and steel strikes, there has been little evidence so far that the economy has been seriously endangered. Certainly the automobile industry—kingpin of industrial health—finds it difficult to sing the blues with any real conviction.

The record flood of automobiles which poured off Detroit assembly lines in August and September almost swamped many retail car dealers and a number of used car dealers quietly slipped under and drowned. There is no doubt that the sellers' market for automobiles is over, although the steel strike and retooling between now and Christmas may restore the balance between output and sales.

Base metal prices have been backing and filling as a reflection of the steel strike and devaluation within the sterling bloc. Lead has dropped steadily to 13¢ a lb under the impact of falling consumption and increased foreign offerings. Zinc dropped to 9.25¢ then moved up to 9.75¢. Galvanizers are out of the market but diecasters and brass mills are buying. Output from three smelters has declined, one because of a strike, and in general supplies of high-grade zinc are tight. Copper so far has resisted downward pressures and remains at 17.62½¢, while copper scrap even has shown a firmer tone. Brass and wire mills and appliance manufacturers have been buying for November delivery, and consumption is estimated as 30,000 tons per month in excess of production and imports.

Beyond the seas, the opportunities of devaluation are slowly bleeding away in England through a lack of forceful action to check inflation at home, to increase labor productivity or to check expenditures for social services in order to partly liberate the economy from its crushing burden of taxation. An increasingly large segment of the voting population is coming to the realization that the Labor Party is incapable of realistically meeting the economic challenge. The resentment is not that Labor is aiming for the social democratic welfare state but rather that the Party is jeopardizing the welfare state through sheer ineptitude. Western Berlin is now in such a state of collapse that it might well become the Achilles heel in the titanic West-East struggle for Germany. And in Japan business men are screaming in anguish as Prime Minister Yoshida applies the screws devised by the Detroit banker, Joseph M. Dodge, to get the Japanese economy off the American taxpayers' back by 1951.

A drama overshadowing all others, however, is rising to frightening crescendo in Yugoslavia. Only 12 years ago the Croat, Josip Broz, was purging the Jugoslav Communist Party of grave heresies then worrying the Comintern. His fondness for ordering people about earned him among his friends the nickname Tito. Now Marshal Tito has defied his old masters and neighbors and turned toward his old comrades, while political trials in Hungary are being staged to prove that the bold heretic of Belgrade is, and always has been, nothing but a Fascist and an enemy of the Soviet Union.



Moscow must make an end to Tito, for he now publicly proclaims that Yugoslavia is leading a worldwide crusade to free the communist countries from Russian slavery. He has just asked his army to die, if need be, for the "working class of the whole world" and declared they are fighting "for a cause which has tremendous and incalculable importance . . . even if we fall . . . things have gone beyond our frontier and will grow . . . the truth blazes." Even the Russian Communist Party itself is now a target for Tito's splitting tactics.

Moscow is beginning to pick off International Brigaders (Spanish Civil War). Rajk (executed in Hungary) was one, and others will soon go down. Tito was the main recruiting agent of the International Brigade in Paris. He and the Brigade members mixed with Trotskyites who also fought against Franco, and the ex-Brigade members are inclined to stick together inside the communist parties.

There will soon be worldwide communist "peace demonstrations" to coincide with the initial military moves against Tito. An attempt will be made to have a few units of the Yugoslav army revolt, to be joined by a new International Brigade fighting under the slogan of "proletarian internationalism" and "defense of the people's democracies against an imperialist-Titoist plot."

In Washington the decision has been made to give Tito "all aid short of war." Power politics being the cynical chess game it is, the battered Greeks soon may be hustling pack trains of American armaments over their bloodied mountains to the country responsible for so many Greek widows.

Fall Dinner, Institute of Meta

Over 400 of the top technical men in the country registered to hear 50 technical papers presented before the regu
17-19. Shown here is the annual Fall dinner, held in the Ballroom of the Allerton Hotel, Tuesday, Oct. 18. The dinn
and their friends and arranged

Electric Furnace Steel Conference Anticipates Record Registration

All indications are that the seventh annual Electric Furnace Steel Conference, to be held in Pittsburgh for the three-day period Dec. 8-10, will attract a record attendance of operating men, repair and maintenance men, metallurgists, ceramic and refractory engineers. Hotel reservations should be made directly with the headquarters hotel, the William Penn, or some other Pittsburgh hotel. There will be a $7 registration fee, which includes a copy of the bound Proceedings when published. Students will not be required to pay a fee unless a copy of the Proceedings is desired, in which case the payment will be $3.00.

The very popular educational session this year will be devoted to the Chemistry of Electric Furnace Steelmaking, a subject repeatedly requested. This session will begin at 9:30 a.m. Saturday, Dec. 10, in the Urban Room. Two motion pictures dealing with steelmaking will precede the principal paper by Charles Locke. Ample time will be provided for questions from the audience, and the panel of experts will include S. F. Carter, Jr., Asst. Melting Supt., American Cast Iron Pipe Co.; E. J. Chelius, Supt. Electric Furnace Dept., Carnegie-Illinois Steel Corp.; G. A. Lillieqvist, Research Dir., American Steel Foundries; W. M. Patterson, Electric Furnace Supt., Allegheny-Ludlum Steel Corp.; Alden Safford, Melting Foreman Chapman Valve Manufacturing Co.; R. J. Wilcox, Technical Director, Michigan Steel Casting Co.

Chairman of the Electric Furnace Steel Executive Committee is Norman I. Stotz, president of Braeburn Alloy Steel Corp.; chairman of the Seventh Conference Committee is J. A. Bowers, of American Cast Iron Pipe Co., and vice-chairman is T. J. McLoughlin of Carnegie-Illinois, Pittsburgh. The local committee on arrangements includes J. W. Harvey, chairman, and Bedell Baxter, T. C. Ford, Grant F. Neely and Willis Shoop.

The Annual Reception and Dinner will be held Thursday, Dec. 8 at 7:00 p.m. James W. Kinnear, Jr., President of the Firth Sterling Steel & Carbide Corp., will act as toastmsater. Gene Flack, Sales Counsel and Director of Advertising of the Sunshine Biscuits, Inc., will be the principal speaker. Cocktails will

Division, Allerton Hotel, Cleveland

ll meeting of the Institute of Metals Div., held in conjunction with the Thirty-First Metal Congress, Cleveland, Oct.
as preceded by a cocktail party in the Chester Room, given with the compliments of the Cleveland members of AIME
e Cleveland Local Committee.

start at 6:30 p.m. in the Urban Room, and as in the past an extremely interesting evening is promised to all.

Details of the entire technical program are as follows:

Registration

Thursday, Dec. 8—Fort Pitt Room
Friday, Dec. 9—Fort Duquesne Room
8:30 a.m.-5:00 p.m.

General Session

Thursday, Dec. 8—9:30 a.m.-9:45 a.m., Ballroom

Welcoming Remarks by J. A. Bowers, Chairman, Committee for the Seventh Annual Conference.

Response by Norman I. Stotz, Chairman, Electric Furnace Steel Executive Committee.

Acid and Basic Technical Session

Thursday, Dec. 8—9:45-12:30 p.m., Ballroom

Materials Handling

Materials handling in the electric furnace shop.
W. G. Nichol, Mgr., Methods Engr. Bureau, Carnegie-Illinois Steel Corp., Pittsburgh.

Preparation of scrap for electric furnace charging.
C. F. Staley, Supt., Electric Fce. Steel Melting Dept., Armco Steel Corp., Middletown.

Fluxes and ferroalloys.
"Handling Electric Furnace Supplies," by Frank C. Weir, Supt. of Material Handling, Steel & Tube Div., Timken Roller-Bearing Co., Canton, Ohio.

Electrodes.
John J. Wyandt, Asst. Supt. Nos. 2 and 3 Melt Shops, Central Alloy District, Canton Steel Works, Republic Steel Corp., Canton, Ohio.

Repairs and maintenance materials, door frames, roof rings.
J. P. Maloney, Asst. Supt. No. 1 O. H., Bethlehem Steel Co., Bethlehem, Pa.

Materials handling in the foundry
(Preprinted) F. O. Lemmon, Asst. Plant Supt., Ohio Steel Foundry Co., Springfield, Ohio.

Temperature and Composition Measurements.

Methods of avoiding stratification in bath.

a—Swedish induction stirring.
(Preprinted) S. Fornander, Res. Mgr., Surahammars Bruks AB and Folke Nilsson, Genl. Mgr., Hagfors Steelworks, Uddeholms AB, Sweden.

b—Reladling.
"Obtaining Uniform Bath Composition by Reladling," by J. J. Green, Melting Dept. Met., Universal-Cyclops Steel Corp., Bridgeville, Pa.

c—Neutral gas stirring.

(Continued on Page 38)

How to Conserve Manganese

by J. C. Vignos

THE current trend of world affairs and its overall effect on the American Iron and Steel industry makes a reappraisal of the manganese problem very timely.

Early in 1949 when the steel producers of this country were cut off by one source of about 40 pct of its manganese ore requirements, conservation of manganese became for the fourth time a very serious problem. The situation was relieved only by the falling off of steel production.

At that time both government and industry were worried and a great deal of careful consideration was given to the manganese problem. What resulted was the setting up of some very worthwhile joint research projects. These projects are under way at present and should contribute greatly to knowledge on the subject and set up a basis for a definite "know-how" for manganese conservation in the future.

J. C. Vignos is vice-president of Ohio Ferro-Alloys Corp., Canton, Ohio. This is one of the papers presented Sept. 30 at Columbus before the National Open Hearth Committee, Southern Ohio Section.

Present steel-making practices have been developed under the high pressure of competition and production and are extremely wasteful of manganese because of both technical or economic reasons.

For each ton of ingots produced it is estimated that the industry is "consuming 36.3 lb of manganese in the form of ores with an additional 6.8 lb coming from scrap reserves, making a total of 43.1 lb of manganese introduced into the steel-making operation per ton of ingots." Annually the steel industry consumes about 680,000 tons of manganese as ferroalloys or about 13.4 lb of metallic manganese per ton of steel.

At present the overall recovery of manganese is about 30 pct. The 70 pct is wasted in ferroalloy furnace slags, blast furnace and openhearth slags. This appears to leave the problem of conservation of manganese wide open for constructive criticism and some improvement.

Blast Furnace Losses—Recycling of Slag: In recycling of openhearth slags only about 70 pct of the manganese is recovered while 100 pct of the phosphorous is retained in the metal, limiting the amount of slag that can be recycled. This loss of manganese is not of too much importance as it comes from a slag that is otherwise headed for the dump. Since under present openhearth operating conditions about 85 pct of the manganese charged into the furnace is lost, the amount of manganese lost in recycling becomes insignificant. But attention should certainly be directed to the more wasteful openhearth slags.

Open Hearth Slags: Recent information obtained from a questionnaire sent out by the American Iron and Steel Institute's Committee on the Conservation of Manganese, to steel plants which represented a total of 65 million tons of steel, gave a weighted average analysis of flush-off slags as follows: Fe = 26.47 pct, Mn = 9.13, SiO_2 = 21.27, and P_2O_5 = 3.60 pct. This represented 4,472,400 net tons of slag.

The finishing slag analyzed: Fe = 16.06 pct, Mn = 5.04, SiO_2 = 14.74, P_2O_5 = 2.37 pct. This represented 7,226,300 net tons of slag.

A total of 772,600 net tons of manganese which is more than the entire amount of standard ferromanganese consumed by the industry points out the very low manganese recovery in the openhearth furnace.

A major factor in this loss is the large amount of manganese lost in the flush-off slags. It is readily acknowledged that the silicon content of the basic iron from the blast furnace controls the amount of the iron charge and slag volume. If the blast furnace could deliver iron to the openhearth consistently under 0.50 pct silicon it would be possible in many cases to eliminate the flush-off altogether. The manganese recovery would then be raised in a single slag process to about 40 pct and the slag volume would be greatly diminished. Further, the sulphur and phosphorus problem would be much easier to handle, fuel consumption decreased and tonnage increased.

Desiliconizing iron with mill scale, iron ore, air or oxygen reduces the manganese content in proportion to the silicon removed. But this should not be too objectionable for the lower carbon grades of steel because it has been shown in the past that high-manganese iron is of little benefit in making these steels. The manganese obtained as a manganese silicate slag in a desiliconizing operation would readily be used in producing ferroalloys such as siliconmanganese alloys suitable for replacing standard ferromanganese.

Should the problem of desiliconizing iron be given more serious attention it is believed that it could be solved by the use of a basic material with air or oxygen in a basic or neutral-lined mixer or converter of some type at not too great an experimental cost.

Assuming that the flush-off slag cannot be eliminated entirely, any reduction in the volume of flush-off slag would greatly increase the residual manganese and lower the manganese losses. Silica and silicon are the controlling factors of slag volume and conservation of manganese.

The treatment of flush-off slags for recovery of manganese has received considerable attention by the Germans who were forced by two world wars to find manganese in slags and slag dumps. The problem of manganese recovery from flush-off slags and finishing slags centers around the elimination of phosphorus.

The Germans made use of two processes based on selective reduction and oxidation for separating the manganese and phosphorus. Openhearth slags were reduced in a blast furnace of the type used for making spiegel producing a metal containing 15 to 25 pct manganese, 1.50 to 4.0 pct phosphorus and about 1 to 2 pct silicon. This metal was then placed in an oxidizing furnace and treated with air and steam to oxidize the manganese and silicon forming a slag and leaving all the phosphorous in the metal. The synthetic slag was then reduced in a ferromanganese furnace to produce an alloy containing 60 to 80 pct manganese. In another process openhearth slags were selectively reduced in a blast furnace to produce a high-phos pig iron and a slag containing a greater portion of the manganese. This slag was then further reduced in a blast furnace to make a ferromanganese containing about 65 pct manganese. In these processes to produce one ton of 65 to 80 pct ferromanganese required 12 to 20 tons of slag with an overall recovery of 60 to 70 pct of the charged manganese. In the emergency, the Germans had to resort to these practices regardless of cost and loss of other iron production. These processes are entirely too costly in terms of tying up equipment in time of an emergency.

Several plans have been presented recently for recovery of manganese from flush-off slags and tap slags that offer some promise. One method proposed is to separate the manganese and phosphorus by selective reduction of the iron and phosphorus in the molten slag with a mixture of carbon and ferrosilicon, the carbon reduction to give turbulence and the ferrosilicon to maintain the required heat balance. The slags from this operation free of phos and enriched in manganese can then be used in a great many ways for recovering the manganese in a form suitable for furnace and ladle additions. Or the slag produced can be treated further while still molten with ferrosilicon to produce a low-carbon ferromanganese. The costs on this operation are attractive today if the recovered manganees is given some credit for its low carbon content.

Of local interest along this line considerable publicity was given in May, 1949, to a process for treating openhearth slags which consisted in grinding these slags extremely fine and by flotation to separate them into an iron-manganese fraction and a high-lime material suitable for agricultural uses. Undoubtedly this invention has been tried on one or more slags and worked. Openhearth finishing slags contain two phases having a large difference in specific gravity—a silicate phase containing the phosphorus in solid solution and an oxide phase containing the iron and manganese. But unfortunately these phases are intimately mixed in a eutectic crystal aggregate. If these slags were allowed to cool slowly and given a chance to crystallize enough during cooling, and it is not too silicious, it could separate into two phases. Metallics and sulphides in the slag would constitute a third and fourth phase. Separation of these from the slag could be done with reagents used for treating sulphide ores. To separate the main two phases would be rather a difficult flotation job and very expensive. It is questionable how many slags can be ground fine enough to be liberated into individual crystals by commercial limits of grinding.

The main object of any manganese addition is to put it into the ingot with as small a loss as possible. Additions are made to the furnace, to the ladle, or both.

Manganese additions to the furnace are for alloying mainly and deoxidation is secondary. Unfortunately, considerable manganese is lost as the result of additions to highly oxidized steels. In rimmed steels with 0.40 to 0.60 pct manganese there is sufficient oxygen left to react with the carbon to give a satisfactory rimming action. The carbon controls the aviable or active oxygen in steels containing manganese at levels below that at which manganese can react.

In killed steels, the more silicon that can be added to the furnace prior to the manganese addition without a phosphorus reversion, the better the manganese recovery. Most openhearth practices on killed steels use only sufficient silicon to hold the heat for the time required. But by adding up to a safe amount of silicon the manganese recovery in the furnace would be increased in proportion. By this practice it is possible to improve manganese recovery from 50 to 70 pct to 65 to 85 pct, depending on the grade of steel being produced.

Ladle additions of manganese should be made whenever possible and to as great an amount as is safe from the quality standpoint. Several plants are now making preparations for ferromanganese additions to the ladles and they will add, depending on the grade of steel, all or a greater part of the manganese in this manner. Recovery will be 7 to 10 pct or better.

The addition of fine ferrosilicon such as ½ in. x down to the stream before it breaks in amounts required to give the desired silicon in the finished steel, will improve recovery of manganese by 4 to 7 pct. When manganese additions are made in the furnace the loss between the tap stream and the metal ingot will average about 5 to 10 pct, depending on how much manganese was added in the furnace. Other alloys are likewise lost during the tapping operation. The use of fine ferrosilicon prevents the air oxidation by surrounding the stream of metal with a highly reducing atmosphere.

Even if manganese additions are made to the ladle, the same method of adding the silicon will give better manganese recoveries because in this method the amount of oxides formed by mixing air and molten metal will be greatly reduced at the expense of silicon. Cost of the silicon is more than offset by improved recovery of manganese or other alloying agents added to the furnace or ladle.

The composition of manganese ferroalloys covers the range of analysis from spiegel to standard ferromanganese of 18 to 82 pct manganese, silicospiegel to silicomanganese of 3 to 25 pct silicon, 18 to 65 pct manganese and 0.02 to 0.25 pct phosphorus. Any analysis falling within the range of these alloys can be used to some extent in more or less amounts depending on the grade of steel being made. This makes it possible to utilize many domestic low-grade ores and flush-off slags, in the manufacture of these alloys.

This matter is being carefully studied and in the event of an emergency, the author believes that the industry will, as in the past, meet the situation without seriously affecting steel production.

The Bessemer Converter

by A. B. Wilder

STEEL has been manufactured by the pneumatic converter process for a period of over one hundred years. The process was independently developed by William Kelly of Eddyville, Kentucky, and Henry Bessemer of England. Bessemer's patent was issued in England and the United States in 1856; and although Kelly did not apply for a patent until 1857, he was able to prove that he had worked on the idea as early as 1847. Kelly was granted a United States patent in 1857.

Lacking financial means, Kelly was unable to perfect his invention and Bessemer, in the face of great difficulties and many failures, developed the process to a high degree of perfection. At first Bessemer employed Swedish ore which was low in phosphorus and high in manganese. The process failed when applied to English ores which were high in phosphorus and low in silicon. In order to save his process in the face of opposition among steel makers, Bessemer built a steel works at Sheffield, England, and began to operate in 1860. Difficulty was experienced with sulphur, which was introduced by the cupola. This objection was overcome by the addition of manganese in the form of spiegeleisen, of which the beneficial effects were first recognized in an English patent by R. Mushet in 1856 and a United States patent 1857.

The first commercial pneumatic converter plant, consisting of a 2½ ton vessel, was erected in this country under the Kelly and Mushet patents, at the Wyandotte Iron Works, Wyandotte, Mich., in 1864, although a Kelly converter was used experimentally at the Cambria Steel Works, Johnstown, Pa., as early as 1861. Alexander L. Holley purchased the Bessemer patent in the United States and in 1865 began at Troy, New York, to make steel. Both interests were later consolidated.

A. B. Wilder is chief metallurgist of the National Tube Co., subsidiary of the United States Steel Corp. of Delaware, Pittsburgh.

In Europe, the bottom-blown basic converter was a natural development due to the fact that the ores were high in phosphorus and it was necessary to remove phosphorus during the blow. This process also produced a slag rich in lime and phosphorus which was suitable as a fertilizer for agricultural purposes. The bottom-blown acid converter was developed in America as the ores were sufficiently low in phosphorus, and bessemer steel produced in this country is manufactured by this process. In Europe, the basic converter process is used for ingot production and the acid converter process is employed in the foundry. The side-blown converter with an acid lining was first successfully developed by A. Tropenas in England and introduced into this ocuntry during the early part of the present century. At the present time, it is used commercially only in steel foundries.

The converter process, extensively used in continental Europe, is known as the Thomas process. Sidney Thomas, an Englishman, obtained a patent in 1879 involving the use of a basic brick lining, a basic flux and the after blow. For the successful removal of phosphorus from high phosphorus ores, all these conditions must be met. Prior to the successful use of a basic lining by Thomas, an acid lining was used in the converter process.

The early use of converter steel in this country involved a considerable quantity of rail steel, and for many years this process was the principal method used for the production of steel. At the present time, the pneumatic process is used principally in the production of steel for buttwelded pipe, free-machining bars, seamless pipe, flat-rolled products, wire, steel castings, and blown metal for the duplex process. The rated converter capacity of the nation is approximately 12,000,000 tons of steel with a considerably greater potential capacity. Over half of this capacity represents blown metal for use in the open hearth or duplex process and the remainder bessemer ingots. Although most of the steel in this country is manufactured by the openhearth process, during the past few years many new converters have been installed and extensive experimental work on converter steel is in progress. The inherent advantages of the process involve economic considerations in times of peace and national security in times of war.

In recent years, fully killed converter steel has been used commercially in the production of seamless pipe and over a million tons of acid bessemer steel have been melted for this application. In addition, over a million tons of dephosphorized acid bessemer ingots have been used recently for welded

Process

THIS is part one of a two-part article in which the author carries the pneumatic converter process from its early history through the most recent technological innovations. In this first part, consideration is given to investment costs, phosphorus and sulphur limitations, scrap market conditions, blowing time, quality and oxidation.

pipe and galvanized sheets. During the last war, the basic-bessemer steel capacity of Germany was an important factor in meeting military demands for steel production. The total production of steel ingots[1] in Germany and occupied countries in 1943 was 38,107,927 net tons. The pig iron produced in the same period was 30,805,605 net tons, or a ratio of ingots to pig iron of 1.24. This may be compared with 88,836,512 net tons of ingots and 55,633,450 net tons of basic and bessemer pig iron produced in this country durnig 1943, or a ratio of 1.7. The ratio of ingot to pig iron production indicates the importance of the bessemer process in Germany during the war. Steel production on a monthly basis in Germany during the war, not including occupied countries, according to process is shown in table I. Bessemer ingots accounted for 43 pct of the production which does not include blown metal for the duplex process.

It is the purpose of this paper to discuss primarily the bottom-blown acid-bessemer process in its relationship to steel making. In addition, certain features of basic and side-blown converter practice will be described. Some of the information presented has been discussed by Price.[2]

ECONOMIC CONSIDERATIONS

Investment Costs: The cost of building a bessemer plant is appreciably less than that of an openhearth plant of equivalent capacity and the difference in cost depends, to some extent, upon the size of individual units. However, in the operation of a bessemer plant, greater blast furnace capacity is required as only a small amount of scrap is used in the process. Therefore, the investment in blast furnace facilities for a bessemer plant would be greater compared to an openhearth plant and must be considered as part of the investment costs. This was probably a factor which was, to some extent, responsible for the shift from bessemer to openhearth production during the past 40 yr.

With proper facilities in an integrated plant, consisting of bessemer converters and tilting or stationary openhearth furnaces, the cost of producing bessemer ingots over a period of years should be less than openhearth ingots. When a shortage of scrap exists and the price is high, bessemer facilities not only have an economic advantage, but are in a better position to meet market demands for steel products. This feature is of considerable importance in time of a national emergency.

Phosphorus and Sulphur Limitations: Iron ores with a low phosphorus content are required in the production of acid-bessemer steel unless dephosphorization is employed. In 1947, the average phosphorus content of bessemer ores was 0.38 pct. The maximum phosphorus content permitted in bessemer ores is 0.045 pct. Availability, therefore, of suitable ores is a fundamental consideration in the successful operation of a bessemer plant unless dephosphorization is employed.

The availability of bessemer ores which do not require extensive beneficiation and concentration in the Lake Superior region is limited. As the industry proceeds toward the use of lean ores requiring crushing, grinding, beneficiation and sintering, the economics involved will affect the bessemer iron situation. Development of taconite deposits in the Lake Superior region which require extensive beneficiation is in progress and will provide additional ores suitable for bessemer steel production. New York State magnetites, low in phosphorus, are also available but frequently contain impurities, including titanium, which must be removed for satisfactory bessemer operations. A suitable method remains to be developed for the removal of titanium. Considerable thought has recently been devoted to the iron ore situation and its relationship to the location of the steel industry. Ore deposits in New York State, Canada, and South America are factors in this situation. Although large quantities of iron ore suitable for bessemer operations are available in Lake Superior region, as the necessity for concentration increases the ores will be more costly. South American bessemer ores will be costly due primarily to handling and transportation costs. Canadian ores may be more attractive. The location of bessemer plants will to some extent be related to the ore situation, but other factors in our economy will probably have a greater effect.

Dephosphorization[3] in the ladle has been successfully used for a number of years in the production of acid-bessemer steel with less than 0.050 pct phosphorus. This is accomplished by adding a mixture of lime, iron oxides and flux, all in the solid state to the bloom metal as it flows into the ladle. Another method for phosphorus removal consists of the well known duplex practice in which a tilting basic openhearth furnace is employed. The technical possibilities of dephosphorization should be more thoroughly developed in the bessemer process.

Sulphur in coke is also an important factor in bessemer steel production as this element is not removed in the acid-bessemer process. If higher sulphur coke is used in bessemer iron production, it is necessary either to remove sufficient sulphur in the blast furnace or resort to other treatments. In the blast furnace, limestone in the charge is adjusted with the burden for sulphur removal. Ladle treatments have been developed in which fused carbonate or sodium hydroxide has been successfully used, particularly with cupola iron. In the duplex process, sulphur may be removed to some extent in the basic openhearth furnace. In Europe, a certain amount of sulphur is removed in the basic bessemer process.

The sulphur problem is approaching a critical position in the steel industry. Sulphur removal in both the bessemer and openhearth operations is rapidly reaching a stage which will require careful economic evaluation. Sulphur is generally an undesirable impurity in steel and is difficult and expensive to reduce. Part of the sulphur in coal is of an organic nature and cannot be removed during coal preparation by any commercial process at the present time. It must, therefore, be removed in the blast furnace or steel works operations. In the future, new methods may be developed not only for the removal of sulphur but also phosphorus in the converter process.

Blast Furnace Improvements: Due to the economic importance of blast furnace operation in the production of bessemer steel, developments in this field are of interest. The use of airconditioning has, in some instances, improved blast furnace operation and high top pressures may be beneficial. Beneficiation and sintering of iron ores and large hearth capacities have also been important technological developments. The possibilities of oxygen-enriched blast are being evaluated in this country. These and other developments will probably improve the bessemer situation by providing iron at a lower cost. Factors of this nature were not involved when the trend in steel production 40 yr ago shifted from bessemer to the openhearth process.

Scrap Market Conditions: The ratio of bessemer to openhearth production is influenced by the availablity of steel scrap. The bessemer process uses about 10 pct scrap. The duplex openhearth process normally utilizes very little scrap while the stationary openhearth process ordinarily employs 35 to 60 pct. Although the quantity of scrap used in the bessemer process is small, this quality may be appreciably increased in the future to approximately 25 pct by oxygen-enrichment of the blast. Further, the use of scrap in the blast furnace may be considered in the bessemer situation.

The bessemer process is more than self-sufficient in scrap. The crop ends in the blooming mill alone produce about 15 pct, and additional scrap is produced in further processing of the material. The stationary openhearth process produces a similar amount of scrap, but constantly uses more than it produces. The deficit is supplied by scrap originating from the bessemer process and out-of-plant sources.

As the tonnage of steel increases, the amount of available scrap will also increase. This increase, however, may not always be in proportion to the steel produced. In the last war, for example, it is estimated that over 170 million tons of steel[4] were sent overseas. In addition, the amount of scrap produced in the steel works processing may be further decreased by technological improvements. During the past few years, less than the desired amount of scrap has been available. Further, openhearth production rates[4] as shown in table II are influenced by the amount of scrap charged.

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[1] **H. M. Brightman, et al, "Friedrich-Alfred-Hutte at Rheinhausen," Office of the Publication Board, Department of Commerce, Washington. Report No. 349, April, 1945.**

[2] **E. G. Price, "The Acid Bessemer Process in the Manufacture of Pipe," American Iron and Steel Institute, Technical Committee Activities, 1948, p. 111.**

[3] **G. M. Yocom, "A Method of Rapid Dephosphorization of Bessemer Steel," Trans. AIME, 1941, Vol. 145, p. 160.**

TABLE I

German Steel Production
(1000 net tons)

	1942			1943									
	Oct.	Nov.	Dec.	Jan.	Feb.	Mar.	April	May	June	July	Aug.	Sept.	Total
Thomas (Bessemer).......	1227	1188	1164	1216	1140	1246	1167	1181	1175	1255	1192	1187	14,338
Openhearth and Electric...	1610	1610	1577	1740	1658	1844	1707	1558	1498	1598	1507	1569	19,423

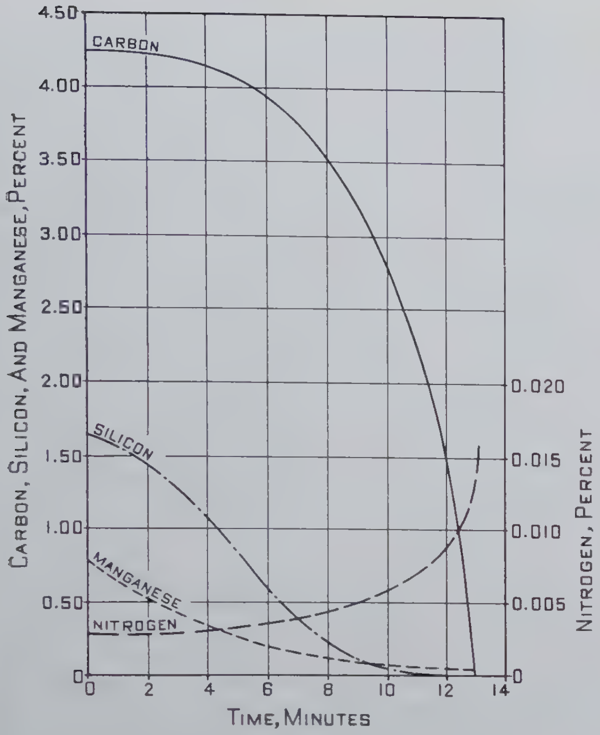

Fig. 1—Typical bath analysis during an acid blow.

The production of bessemer steel is apparently not great enough at the present time for the correct balance of processes in the steel industry. This is particularly true in the individual steel plant which does not have integrated bessemer and openhearth facilities. If the present unbalanced condition continues for a sufficient period, economic pressure may bring about conditions which will result in increased Bessemer production. The economy in Europe prior to the war resulted in appreciable bessemer production which was not only due to high phosphorus ores but also the limited amount of scrap.

The bessemer process has certain economic advantages when scrap is scarce and costly, but there are periods in the U. S. economy when scrap is plentiful and cheap. Therefore, the economic pressure which exists over a period of years will be a major factor which influences the bessemer steelmaking capacity of the nation.

Metal Losses: Metallic yield in the bessemer process is comparable with stationary and duplex openhearth practices and is influenced by metalloid losses, oxidation of iron, slopping and other operating characteristics. Depending upon facilities and operating conditions, the performance of acid-bessemer plants in terms of metal yield has been similar to openhearth plants.

Blowing Time and Quality: One of the important economic factors in the production of bessemer steel is that a blow usually lasts for a period of only 10 to 15 min. However, the time required to make a certain quantity of steel depends on size of the vessel, and converters in this country are relatively small. Due to the fact that the time required to make an acid-bessemer blow is relatively short, the problem of controlling quality of the product differs somewhat from openhearth practice. Speed of the operation is so rapid that the necessity for certain control measures differs from those required by the openhearth melter. The bessemer process, to a marked degree, is automatic in its operation.

Typical changes in bath composition during an acid-bessemer blow are shown in fig. 1, after King.[5]

The composition of the steel cannot be regulated satisfactorily by stopping the blow at an intermediate point due to the speed of reactions and other conditions. It is possible to blow a bessemer heat to several carbon levels, but a more uniform product in chemical composition is obtained by blowing to the drop of the flame and adding carbon and managanese as required. High-carbon blown metal is sometimes produced in the duplex process as further refining and adjustment in chemical composition are made in the openhearth furnace. At the first indication of a drop of the flame and other changes in appearance of the flame, the converter may be turned down "young," and the carbon content will be approximately 0.10 pct. However, most of the acid-bessemer steel is blown "full" to insure uniform composition. The vessel is turned down as height of the flame continues to decrease and certain changes in appearance are observed. Full-blown heats contain approximately 0.04 pct carbon. If the manganese content of the metal at the beginning of the blow is too high, a fluid slag which contributes to "slopping" is produced. Therefore, the ratio of silicon to manganese must be controlled. Silicon is also a source of heat and therefore an important factor in temperature control during the blow.

In the bessemer process, characteristics of the flame at the end of the blow and the deoxidation practice employed are fundamental factors which control quality of the product. The additions required to produce various grades of acid-bessemer steel are incorporated in the deoxidation practice and may be added to the vessel, ladle, or mold.

Control of the bessemer operation is being constantly improved. Experimental work on the measurement of temperature is in progress. In certain instances, radiation characteristics are being determined by the use of a photocell or spectroscope for end-point control. New methods are being de-

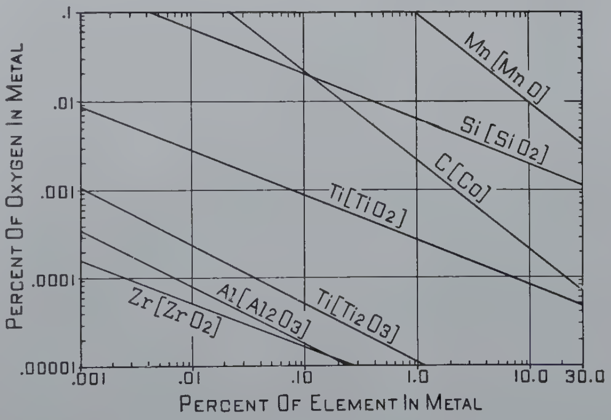

Fig. 2—Equilibrium between oxygen and other elements in liquid steel at 1600°C (2910°F). FeO = 4.49 (O).

veloped to evaluate iron quality in terms other than chemical composition. Experimental work is also being conducted on deoxidation practices and variations in procedure for blowing the metal. These and other factors will provide better quality control of the product.

DEOXIDATION OF STEEL

General: In the deoxidation of bessemer steel, the oxygen content of the blown metal is one of the significant factors involved. The iron-oxide content is also related to the nitrogen content in that both are increased by higher temperatures and overblowing. In the production of killed-bessemer steels, the deoxidation practice must also take into consideration the fixation of nitrogen. Therefore, for proper deoxidation, it is essential to control carefully the temperature and end-point of the bessemer blow.

The equilibrium proportions of oxygen in molten steel at 1600° (2910°F) with various deoxidizers are shown in fig. 2 after Chipman. The amount of oxygen shown in fig. 2 does not necessarily indicate the true deoxidizing power of the several elements. The activity coefficient of oxygen in molten steel may be less than unity and depends, according to Chipman, not only upon temperature and the amount of deoxidizer present but also upon the nature of the deoxidation product. This is another way of stating that the behavior of oxygen in molten steel as expressed by the law of mass action is dependent upon the oxygen activity rather than its concentration.

The concentration of dissolved oxygen in excess of that which would be in equilibrium with carbon and with carbon monoxide at a partial pressure of one atmosphere is not considered in fig. 2. This excess oxygen Δ [O], in liquid steel varies from about 0.009 to 0.35 pct oxygen by weight in the openhearth process according to Brower and Larsen.[6] The amount of oxygen in acid-bessemer steel from the data of McGinley and Woodworth[7] shown in fig. 3 is in excess of the equilibrium value. Further, the influence of temperature on the oxygen content of steel is extremely important. Carbon, for example, is a more powerful deoxidizer than silicon or manganese at a temperature of 1600°C (2910°F) when the carbon content of the bath exceeds 0.10 pct. This is shown in fig 2.

Rimmed and capped acid-Bessemer steel is usually fully blown and finished with a low carbon content. These steels are not completely deoxidized and, therefore, a strong evolution of gas occurs during solidification in the mold. Sufficient deoxidizer may be added, either in the ladle or mold, to control action in the mold. In capped steels, the period of gas evolution in the mold is further controlled by using a steel cap which chills and solidifies the top of the ingot. Steel of this type usually contains about 0.07 pct C, 0.45 pct manganese, 0.08 pct phosphorus, 0.025 pct sulphur and 0.005 pct silicon. In the manufacture of killed acid-bessemer steel, strong deoxidizers, including carbon, ferrosilicon and aluminum are added to the molten steel at the end of the blow. Ingots with a dense homogeneous structure relatively free from porosity or blowholes are produced from killed steel. Steel of this type may contain 0.10 pct or more carbon, 0.35 to 1.25 pct manganese, 0.10 to 0.30 pct silicon, 0.08 pct phosphorus and 0.025 pct sulphur. Alloys may also be added if desired. The factors responsible for the superior quality of deoxidized acid-bessemer steel as compared with rimmed or capped bessemer do not depend entirely on the fact that a killed steel is involved, but more precisely, in the method of killing the steel.

Carbon Deoxidation: The deoxidation characteristics of carbon under equilibrium conditions are shown in fig. 2. In addition to the oxygen in equilibrium, Δ [O] which is the oxygen content of the metal in excess of equilibrium value, is a factor.

TABLE II

Influence of Hot Metal on Openhearth Production Rates

Pct Hot Metal	Tons per Hr (150-Ton Furnaces)
40	10.1
45	11.0
50	11.9
55	12.9
60	13.9
65	14.9

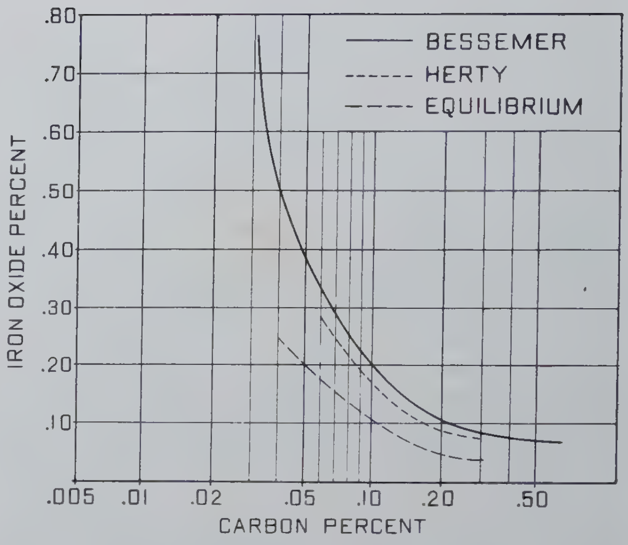

Fig. 3—Relationship between carbon and iron oxide content of bessemer blown metal.

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[4] R. L. Fetters, et al, "Effect of Raw Materials on Steelmaking," American Iron and Steel Institute, Technical Committee Activities, 1948, p. 47.

[5] C. D. King, "Seventy-five Years of Progress in Iron and Steel," AIME, 1948, p. 108.

[6] T. E. Brower and B. M. Larsen, "Oxygen in Liquid Open Hearth Steel—Oxygen Content During the Refining Period," Trans. AIME (1947), 172, p. 137.

[7] E. E. McGinley and L. D. Woodworth, "A Study of Modern Bessemer Steels," Trans. AIME (1941), 145, p. 151.

[8] H. E. Work and G. Enzian, "Effect of Deoxidation on the Strain Sensitivity of Low Carbon Steels," Transactions of AIME (1945), 162, p. 723.

The oxygen content of rimmed or capped acid-bessemer steels is high and must, to a certain degree, be evaluated by behavior of metal in the mold. These steels are generally low in carbon, and carbon deoxidation is not an important factor in the production of "open" steels.

The carbon content of killed bessemer steel varies from 0.10 pct to the level desired, depending upon the grade of steel. A sufficient amount of deoxidizer is added to produce a steel which has no action in the mold. In order to meet carbon requirements and properly deoxidize the steel, molten blast furnace iron containing about 4 pct carbon is added to the vessel at the end of the blow. After the addition of hot metal, a reaction takes place for several minutes in the vessel which results in the formation of carbon-monoxide gas. This is similar in some respects to "blocking" a heat except that the mixing of blown metal and hot metal is almost instantaneous. The carbon-monoxide burns at the mouth of the converter. Removal of oxygen as a gas not only deoxidizes the steel but removes oxygen immediately instead of forming a solid non-metallic inclusion which must rise to the surface of the steel. Steel made by this process is distinctly different from regular acid-bessemer steel. The steel contains fewer non-metallic inclusions than if silicon or aluminum had been added before the carbon reaction.

In the use of hot metal for deoxidation of acid-bessemer steel, provisions must be made for accurate weighing of the addition. Other means may be used for carbon deoxidation in which solid materials are added, but the simplest and most thorough method at the present time is the use of hot metal.

Manganese and Silicon: In the manufacture of killed bessemer steels, manganese and silicon may be added after carbon deoxidation either to the vessel or ladle in sufficient quantity to provide the amount desired in the finished steel. Additions to the vessel are preferred and are accomplished by the use of a chute which is shown schematically in fig. 4. Usually, 75 pct ferromanganese and 50 pct ferrosilicon are employed. Special types of deoxidizers containing silicon and/or manganese with aluminum have been successfully used. In the manufacture of rimmed or capped bessemer steels, silicon is seldom used, and manganese is added to the ladle for fixation of sulphur and to improve rolling characteristics. The efficiencies of the various additions are similar to openhearth practice at the same carbon level.

TABLE III

Appropriate Nitrogen Content During An Acid-Converter Blow

	Carbon, Pct	Nitrogen, Pct
Hot metal	4.25	0.004
Start C flame	3.50	0.005
Max C flame	2.50	0.005
Prior first change	0.12	0.014
End of blow	0.04	0.013
Ladle	0.06	0.015

Aluminum Deoxidation: Aluminum or its equivalent is used in the production of killed bessemer steels, and it will be observed in fig. 2 that it is a very strong deoxidizer. Aluminum is added in killed steels after carbon and silicon have removed most of the oxygen. Aluminum additions for killed steels are made to the ladle, and a sufficient quantity in the form of notched bars is added to insure fine grained deoxidation practice. For killed bessemer steel containing about 0.15 pct carbon, 3 lb of aluminum per ton of steel are added to the ladle, and for steel containing about 0.35 pct carbon, 2 lb of aluminum per ton of steel are used. In the production of rimmed or capped bessemer steels, very little aluminum is used, and it is normally added as pellets to the mold during teeming. Various methods have been used for adding aluminum to steel. The development of a superior method for making this addition would be desirable.

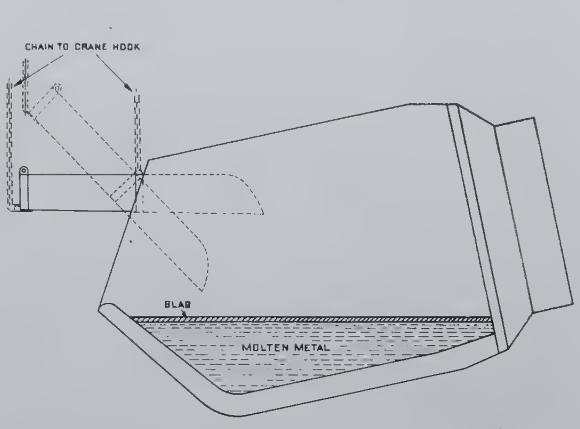

Fig. 4—Arrangement for adding ferroalloys to the bessemer converter.

Although aluminum is primarily added to steel for deoxidation purposes, it is also used for nitrogen fixation in killed bessemer steels. The fixation of nitrogen in killed acid-bessemer steel with aluminum or other elements imparts to this steel superior toughness and notch-sensitivity characteristics. The proper use of aluminum or its equivalent is essential in the production of a satisfactory killed bessemer steel.

Under normal operating conditions, the nitrogen content of bessemer steel at the end of a blow in a 25-ton bottom-blown acid-converter is 0.015 pct nitrogen, as shown in table III. This nitrogen content is similar to many heats of electric steel. Except when made to coarse-grained deoxidation practice, electric steel is usually killed with aluminum and the nitrogen present is frequently combined with other alloying elements. In the manufacture of aluminum killed bessemer steels, the behavior of nitrogen in the finished product is controlled by the addition of aluminum to the steel which results in the formation of aluminum nitride.[8] It is therefore possible to produce a killed bessemer steel with 0.015 pct nitrogen which is similar to ordinary openhearth steel.

Next month the author will conclude this article with detailed discussions on technological developments, which include converter design, oxygen-enriched blast, end-point evaluation and temperature control.

Solid-Phase Bonding of Aluminum Alloys to Steel

THE best known methods of bonding aluminum to steel are probably those which involve a liquid phase in the aluminum. For example, casting, brazing, and hot dipping have been developed by Sheshunoff and his associates within the past ten years.[1] These methods are characterized by formation of intermetallic compounds which cause brittle, low-strength bonds. A method of seam welding copper to aluminum has been recently described by Gillette.[2] This technique minimizes the copper-aluminum phase by squeezing it out while molten.

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Solid-phase methods for bonding aluminum to steel have been comparatively scarce. R. Hess has developed a technique for seam welding aluminum sheet to silver plated steel.[3] This method probably forms a liquid phase for an extremely brief time. Various electroplating methods have been developed for plating iron, nickel, chromium, copper and other metals on aluminum. Aluminum-clad steel sheet has been produced by the roll-cladding process for the manufacture of bearings. Merritt and Keller have a patent on roll cladding aluminum to stainless steel sheet.[9] The Germans have developed a similar process (Feran).[4] These procedures definitely involve solid-phase bonding, as do all roll-cladding processes.[5] G. E. Co. Ltd., has developed a method of cold-pressure welding aluminum alloys to each other or to copper and nickel, but make no mention of bonding steels to aluminum.[6]

High mutual solubility between two metals in the solid state is commonly considered very desirable in solid-phase bonding for the formation of a strong bond. It may not be commonly realized that strong bonds can also be produced between two rather dissimilar metals such as iron and aluminum. They form brittle phases if bonding is performed at too high a temperature or if attempts are made to solution heatreat the aluminum alloy according to conventional practice.

Durst[7] has indicated that strong bonds often may be formed in metals which are greatly dissimilar, and he described a few experiments to justify this. His description of shearing two metals

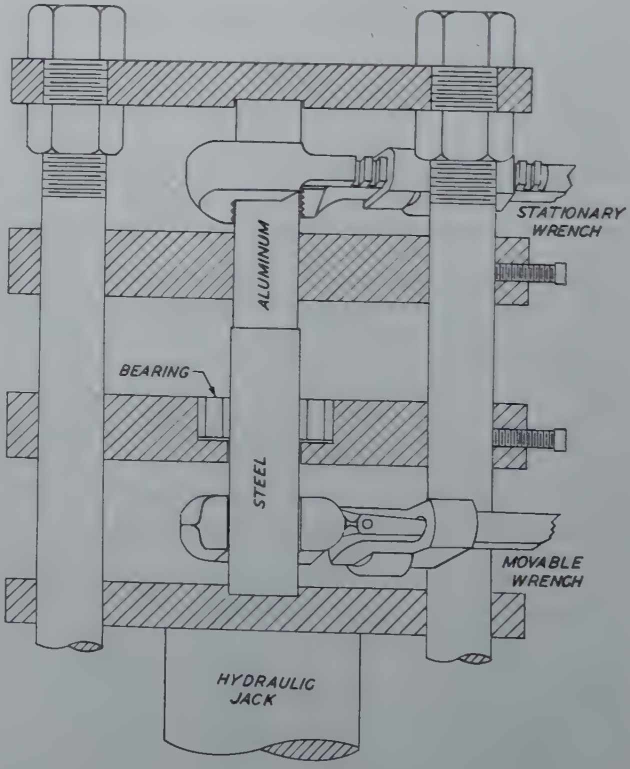

Fig. 1—Press used for twisting aluminum bar against steel.

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[1] "Processing of Aluminum-Steel Bonded Assemblies," M. G. Whitefield, V. Sheshunoff, Modern Metals, April, 1948.

[2] "Copper-Aluminum Joints and Combinations Made by Upset Welding," R. T. Gillette, Materials and Methods, July, 1948.

[3] "A Method for Welding Sheet Aluminum to SAE 4140 Steel," W. F. Hess, E. F. Nippes. Welding Research Council of Eng. Foundation, March, 1946.

[4] "Aluminum Clad Strip," Miller & Hahn. Iron and Steel, v. 21, February, 1948.

[5] "Clad Steels," Materials and Methods, September, 1947.

[6] "Cold Welding of Aluminum," Aircraft Production, June, 1948; Light Metals, July, 1948.

[7] "A Few Observations on Solid-Phase," Durst. Metal Progress, January, 1947.

against each other by means of a vise and chisel to produce a bond suggested twisting as a possible mechanism for bonding aluminum to steel. Accordingly, tests were conducted to prove the validity of such reasoning. The majority of tests were conducted with 32S and B18S aluminum alloys being joined to stainless steels of the 18-8 type, such as AISI 303, since the latter was considered particularly desirable for an ultimate application. The comparatively good results obtained with twisting tests led to investigation of hot press and shear techniques, and these were found to give results comparable to those obtained by twisting.

Twisting Procedure: Materials used were as follows: Specimens of 32S alloy machined from 3 in. diam extruded bars; 17S specimens from 1 in. hot-rolled bar; and B18S specimens machined from 1 in. square swaged bars. These alloys were used in the annealed condition unless otherwise noted. AISI 303 stainless steel specimens were machined from annealed 1 in. diam rolled barstock.

by V. W. Cooke and A. Levy

ONE well-known technical man has said to the authors "Everyone knew it was impossible so you went ahead and did it." This is the first description of three procedures for solid-phase bonding of aluminum alloys to various steels, the bond strengths being very high. From this beginning a whole new series of composite metals may follow.

Nominal compositions of alloys used for twist, press, and shear tests are shown in table I.

After suitable surface preparations, specimens 1 in. in diam by 6 in. in length were placed end-to-end in a press equipped with aligning jigs (fig. 1). Preliminary work established the following general procedure. Pressure was maintained at approximately 5000 psi while specimens were being heated by a gas-air torch. Temperature was measured either by a surface contact pyrometer or an iron-constantan thermocouple embedded in the steel near the bond interface. When a temperature of 500°F was reached, pressure was decreased to 1500 psi and this pressure was maintained until the desired bonding temperature was attained. At this point, the pressure was increased to the desired value simultaneously with twisting of the steel specimen by means of a Stillson pipe wrench. Pressure had to be continuously applied during the twist period to avoid decrease caused by upsetting of the aluminum alloy. Twisting of the steel bar was usually carried out over an arc of at least 180° and some spiral grainflow was formed in the aluminum alloy. A typical twist-bonded specimen is shown in fig. 2a.

After twisting, the specimens were cooled to 500°F and removed from the press. They were then subjected to various heatreatments prior to tensile testing for bond strength, fig. 2b. Solution heatreatment or annealing of bonded samples was carried out in a Lindberg tempering furnace with circulating air atmosphere. Samples were air blast quenched after solution treatment by means of an air jet at 80 psi (3/8 in. orifice) directed at the free end of the steel bar from a distance of 18 in. Some lag was evident in the cooling of the stainless steel bar compared with the aluminum, as would be expected. Several trials were made with water quenching, salt-bath quenching, or varied positions of the bonded bars with respect to the air blast.

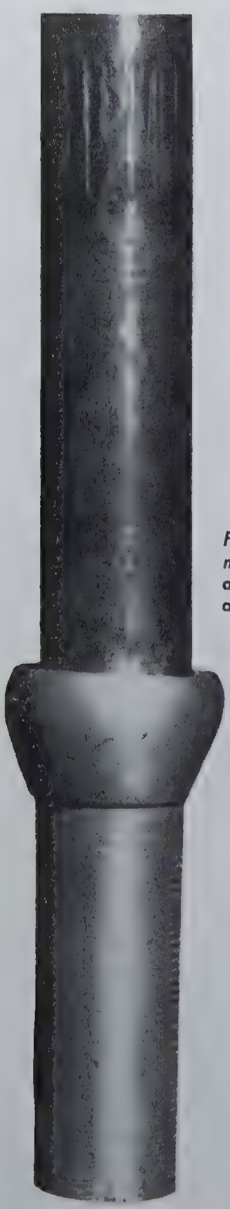
Annealing treatments normally consisted of 2 hr at heat (750°F-850°F) followed by air-cooling. However, some treatments employed a furnace cool from 850°F to 500°F to avoid solution treatment.

Hot Press Procedure: Specimens of 32S alloy were machined from 3 in. diam extruded bars. B18S and RR58 specimens were cut from 1 in. square swaged bars. A51S specimens were machined from 3 in. diam hand forgings. X-750 specimens were taken from cast slugs 2 in. in diam by 10 in. long. After suitable surface preparations, specimens 1 in. diam x 1 in. long of various materials were assembled in sleeve dies, as shown in fig. 30. Heat was supplied by a gas-air torch and controlled by either a contact pyrometer or a thermocouple inserted in the base die. Pressures of 2000-3000 psi were maintained from 70°F until bonding temperatures were reached, and then increased to actual bonding pressures. Dies were of hardened high-speed steel, lubricated by a mixture of oil and graphite. The lubricant was burned off until smoking ceased, prior to use. This was important in order to avoid contamination of interface bond areas by carbon.

After holding at heat for 5 min, the specimens were cooled and then removed from the dies by pushing out through a ring. Bonded specimens were then subjected to various heatreatments and machined into tensile specimens, fig. 4. The same heatreating equipment was used as in the twisting tests.

Peel-test specimens were also bonded in these dies. Disks of test steels, from 0.020 to 0.060 in. in thickness, were bonded to the desired aluminum alloy, heatreated, and then peeled by means of a chisel and hammer as a quick evaluation of bond strength and adherence. These tests were usually tried prior to bonding of tensile specimens since they quickly eliminated undesirable combinations.

Shear Procedure: Bars of AMS 5700 steel 9/16 in. in diam were machined with tapers varying from 2° to 10°. Blocks of 18S aluminum alloy (3 in. square, cut from hot-rolled slab) were faced off with parallel flats and then holes were drilled with tapers to match those of the steel bars and



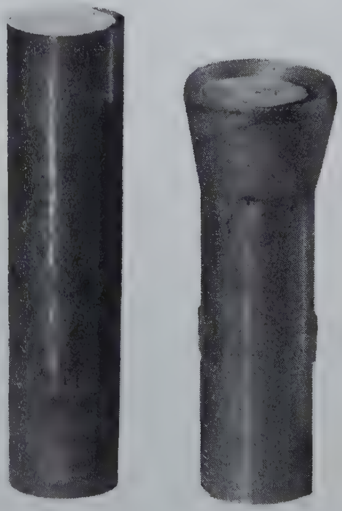
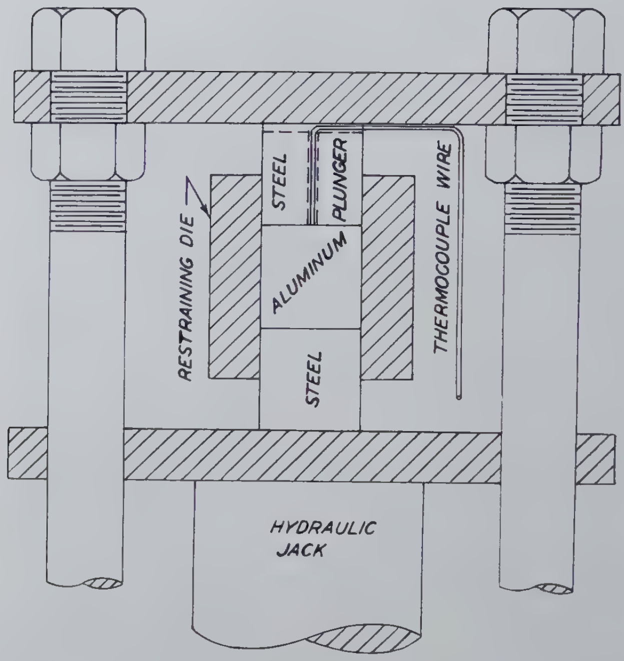


Fig. 2—Typical specimens of 32S aluminum bonded to AISI 303 steel by twist at 550° F: a—(left) before tensile test, actual size; b—(below) after tensile test, two-thirds actual size.

Fig. 3 (Right)—Press and dies used for hot-press bonding of aluminum alloys to steel.



with interference fits of 0.020 in. (fig. 5a). Specimens then were assembled loosely without pressing together, preheated to bonding temperature either in a furnace or by a gas torch (flames were kept away from the area to be bonded). After heating, they were inserted in sleeve dies and pressed until bonded. Bonded specimens then were heatreated and machined so that the shoulder of the 18S block was square with respect to the bar. Shear strength of the bond was obtained by pulling the specimens in a tensile machine. A typical shear-test specimen after failure is shown in fig. 5b.

Twist Bonding

Surface Finish: A few test results which give some idea of the effect of various surface treatments on tensile bond strengths of twisted samples are shown in table II. They cannot all be accepted as typical values since in some cases only one or two tests were run. In general, there were a number of cleaning procedures which gave intermediate

TABLE I

Nominal Composition (Pct) of Various Materials Used for Tests Aluminum Alloys

Aluminum Alloys

	Cu	Ni	Si	Mg	Cr	Fe	Mn	Ti	Al
17S	4.0	...	...	...	...	...	0.5	...	bal.
18S	4.0	2.0	...	0.6	...	...	...	...	bal.
B18S	4.0	2.0	0.7	1.5	...	...	...	...	bal.
32S	0.9	0.9	12.2	1.1	...	...	...	...	bal.
A51S	...	...	1.0	0.6	0.25	...	...	...	bal.
RR58	2.0	1.2	0.05	1.6	...	1.2	...	0.18	bal.
X-750	1.0	1.0	(Sn 6.5	...	...	...	...	...	bal.

Steels

	C	Cr	Ni	Mo	Se	Ti	Fe
AISI 416	0.15 max	13.0	....	0.60 max	0.20	....	bal.
AISI 414	0.13	13.0	1.5	....	....	....	bal.
AISI 303	0.15 max	18.0	9.0	0.75 max	0.25	....	bal.
AISI 321	0.08 max	18.0	10.0	0.50 max	....	6 x C	bal.
AISI 310	0.09	25.0	20.0	....	....	....	bal.
AMS 5700 (TPA valve steel)	0.45	13.0	13.0	0.40	....	W 2.0	bal.
SAE 4340	0.40	0.8	1.8	0.25	....	....	bal

TABLE II

Effect of Surface Treatment Upon Bond Strengths of Several Aluminum-Stainless Steel Bimetals

Specimen No.	Condition		Tensile Bond Strength, PSI
	Aluminum	AISI 303 Steel	
	As Twisted at 850°F and 6500 PSI		
19, 115, 116	17S etch 20 pct NaOH solution	50 pct HCl macroetch	3000–6000
42	17S, fine lathe cut	fine lathe cut	9400
10	17S, lapped, 3-0 emery	lapped 3-0 emery	11,800
52, 54	17S, etch 20 pct NaOH solution	lapped 3-0 emery	9170–16,800
749, 751	32S, No. 50 grit, pre-oxidized 1 hr at 850°F	3-0 emery, anodic etch in 75 pct H_3PO_4	21,000–26,000 (annealed)
750	32S, No. 50 grit, pre-oxidized 1 hr at 850°F	3-0 emery, anodic etch in 75 pct H_3PO_4	38,300 (heatreated)
	Twisted at 550°F and 12,000–25,000 PSI, annealed at 850°F		
714, 715	32S, No. 24-grit belt grind	3-0 emery, anodic etch H_3PO_4	15,300–17,000
352	32S, wire brushed	3-0 emery, anodic etch H_3PO_4	20,700
372	32S, rough lathe cut	3-0 emery, anodic etch H_3PO_4	25,000
360, 363	32S, No. 50-grit belt grind	micropolish	28,000
278	32S, etch 20 pct NaOH dip HNO_3	3-0 emery, anodic etch H_3PO_4	24,000*
264	17S, etch 20 pct NaOH, dip HNO_3	3-0 emery, anodic etch H_3PO_4	24,000*
267, 268	B18S, etch 20 pct NaOH, dip HNO_3	3-0 emery, anodic etch H_3PO_4	24,000*

* Consistent proof tests.

bond strengths. A certain amount of surface roughness apppeared to be important for the aluminum alloys. Grinding on a No. 50 grit belt gave the greatest consistency as well as the highest bond strengths. Deep macroetching in 20 pct sodium hydroxide followed by a dip in concentrated nitric acid and a water rinse also was quite effective, and would be more practical for parts of varying contours. Anodic etching of a smoothly polished surface of AISI 303 steel produced the best bond strengths.

Some tests were run on samples with preoxidized surfaces. Preoxidation up to 850°F for 1 hr or less had no measurable effect upon bond strengths of twisted samples.

Effect of Twisting Temperature on Bond Strength: B18S and 32S aluminum alloys were hot-twist bonded to AISI 303 steel over the range of 550°F to 850°F (fig. 6). The optimum temperature for highest bond strength, as twisted, was found to be approximately 700°F for B18S and slightly lower for 32S alloy. Actually, it was found preferable to twist at lower temperatures (around 550°F), then anneal at 750°F-850°F to improve the bond strength, because the lower twisting temperatures provided the advantages of less upsetting or spiralling of grainflow during twisting. Twisting at temperatures below 500°F tended to cause difficulty with ruptures and edge cracking in the aluminum. Therefore, comparatively little work was done in this range.

The low-bond strength of specimens as twisted is believed due partly to high residual stress. Tensile fractures of bars twist-bonded at 500°F usually showed considerable aluminum adhering to the steel, with fractures tending to progress along 45° shear planes due to excessive straining of the aluminum. Subsequent annealing at 650° F to 700° F caused recrystallization.

Effect of Pressure on Bond Strength: Pressures of 12,000 to 13,000 psi were used for the majority of twist tests at 550°F (fig. 7). It was found possible to maintain such pressures on unconfined bars up to temperatures of approximately 700°F without excessive upsetting. At a temperature of 850°F, a pressure of 6500 psi

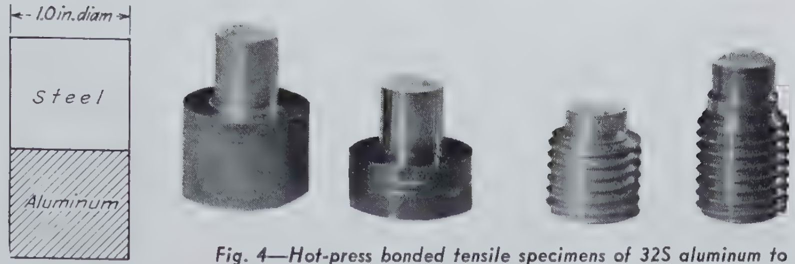
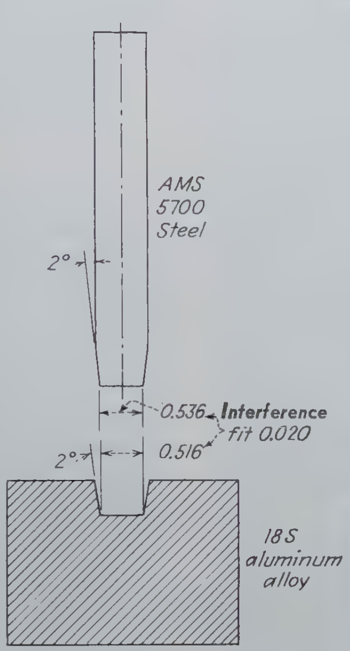


Fig. 4—Hot-press bonded tensile specimens of 32S aluminum to AISI 303 steel: a—(left) dimensions prior to bonding; b—(above) after tensile test.



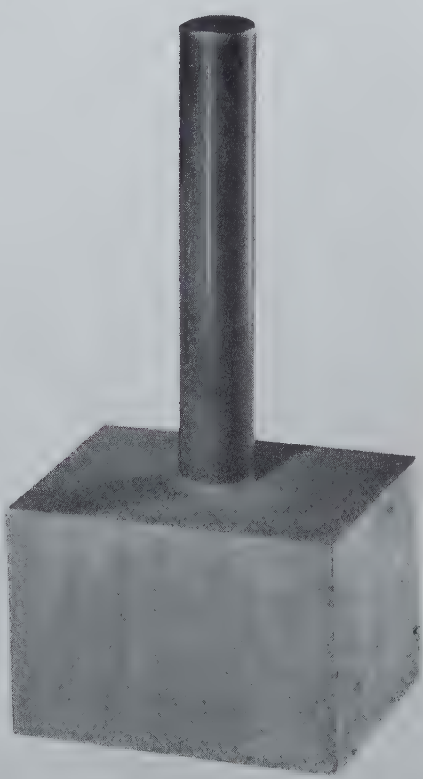


Fig. 5—Dimensions of shear-bond specimen, a—(above); b—(right) typical shear-test specimen of AMS 5700 steel bonded to 18S aluminum alloy.

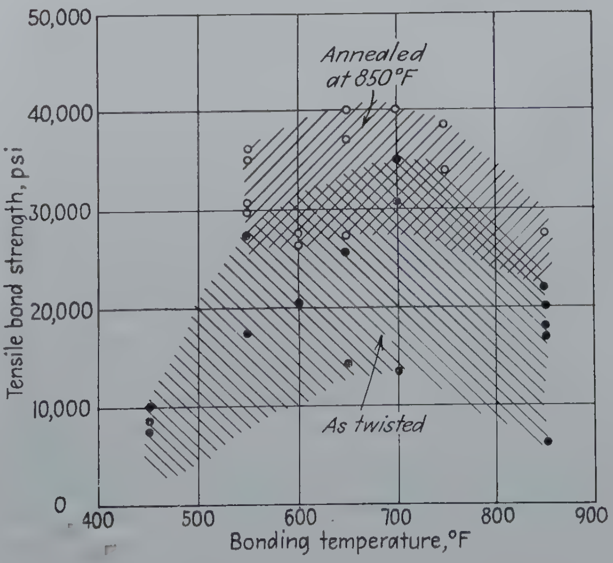


Fig. 6—Effect of twist temperature and subsequent anneal (850° F) on bond strength of B18S aluminum to AISI 303 steel.

was the highest that could be maintained, and even this caused considerable upsetting and was probably responsible for some inconsistency in bond strengths.

Amount of Twist: Comparatively little was done to investigate the amount of twist required for good bonding. Actually, it is believed that the major function of the twist is to provide complete contact and more uniform pressure of the aluminum against steel. If a relatively small amount of twist was used, bonding was often incomplete. Several separate twists, with accompanying reheating, were used for each specimen. Each twist amounted to about 45°, although perhaps only half of this was actual relative slip at the interface. The remainder of each twist merely produced spiral grainflow in the aluminum. The total twist normally used for effective bonding was at least 1 in. of slip at the interface at the OD of bars.

Effect of Subsequent Heatreatment Upon Bond Strength: Annealing at 750°F to 850°F (and air cool) after twist-bonding below 700°F was found to increase bond strength and provide greater consistency of test results. Reference to fig. 6 shows that a large increase in bond strength of B18S to AISI 303 steel can be expected by annealing at 850°F after twisting at 550°F. Annealing at 850°F was also found to insure higher bond strengths in samples that had been twist-bonded above 700°F.

When twisted at temperatures below 700°F, the aluminum alloys become highly strained near the bond interface. Spiralling of the grainflow was quite evident. Edge cracking and internal ruptures occurred on samples twisted below 550°F, particularly in B18S alloy. Subsequent annealing at 850°F caused grain refinement in the aluminum adjacent to the interface and resulted in high bond strengths.

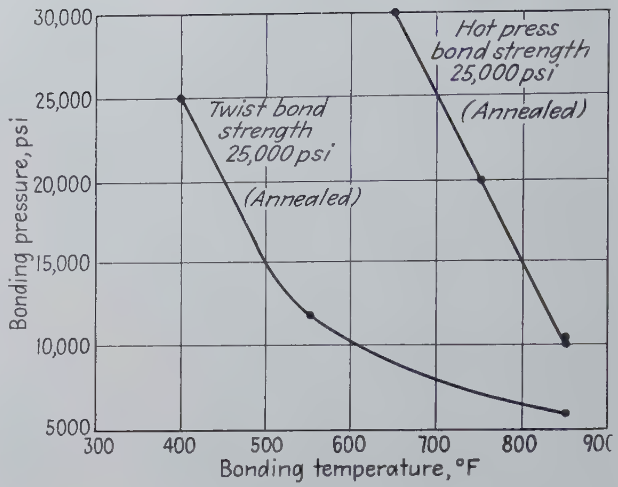


Fig. 7—Minimum pressures required to obtain consistent bond strengths of 32S bonded to type 302 steel.

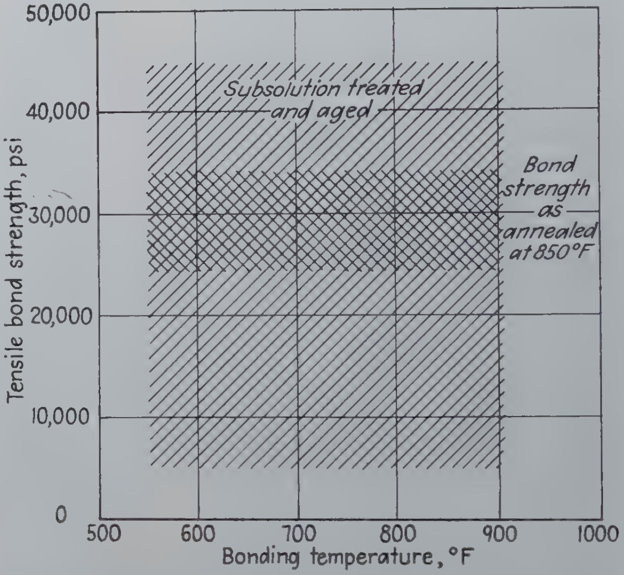


Fig. 8—Effect of subsolution heatreatment, air-blast quench, and 450° F age upon bond strength of 32S aluminum alloy to AISI 303 steel.

Several tests indicated that annealing after twist bonding of 32S alloy could be performed as low as 650°F if the time was increased to 24 hr. The temperature of 850°F was selected chiefly to be sure of complete recrystallization and stress relief, although it was realized that some solution of constituents does occur. It was found that hot-twist bonded assemblies of 32S to AISI 303 steel could be subsolution treated at 930°F, airblast quenched, and aged at 450°F without failure of the bond (fig. 8). A solution treating temperature of 950°F appeared to be the maximum that could be used, and 920°F was considered the optimum temperature to avoid weakening of the bond due to alloying. The solution-treating temperatures normally recommended for 18S and 32S alloys are 940°F and 950°F, respectively. A photomicrograph of 32S twist-bonded to AISI 303 steel, after 2 hr at 930°F is shown in fig. 9. When solution-treating temperature, quenching and removal of hot samples from dies were not carefully controlled, pronounced lowering of bond strengths resulted. Although bond strengths of solution-treated and aged samples sometimes exceeded the strengths of the aluminum alloys, they tended to average considerably less. The annealed bonds, however, were consistently as strong as the annealed aluminum alloys.

If solution-treating temperatures above 950°F were used, alloying occurred quite rapidly with formation of brittle iron-aluminum phases. Under such conditions, bonds were weakened or destroyed.

The amount of iron-aluminum phase formed during six hours at 950°F is shown in fig. 10. When sufficient alloying was present to destroy the bond, the iron-aluminum phase was revealed in the fracture at the interface. Bond strengths of bimetal samples, after solution heatreatment only, were surprisingly low, although these data are not shown. Full aging of the aluminum for prolonged periods (24 hr or more) at 340°F still did not pro-

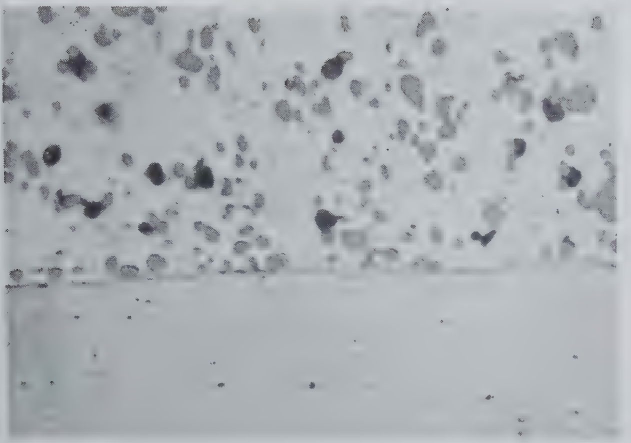


Fig. 9—Aluminum (32S) twist-bonded to AISI 303 steel at 550° F, solution treated 2 hr at 930° F, air-blast quenched, and aged 2 hr at 450° F.

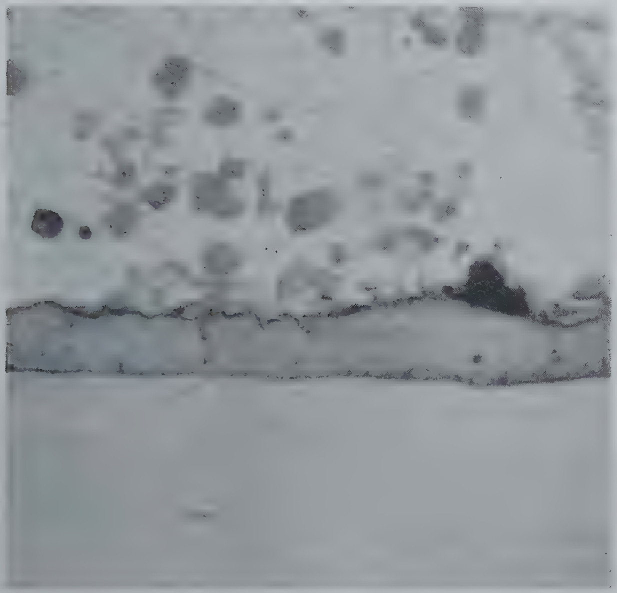


Fig. 10—Aluminum (32S) twist-bonded to AISI 303 steel at 850° F, solution-treated at 950° F for 6 hr, aged 2 hr at 450° F, showing iron-aluminum phase at interface. Keller's etch, 1000 X.

vide sufficient stress relief to raise bond strengths. However, aging at higher temperatures, such as 450°F, for 1½ hr was found to bring bond strengths up to levels shown in fig. 9. Such results illustrate the important effect that residual stress may have upon bond strength.

Effect of Variations in Composition: Table I shows nominal compositions of various alloys used for tests: 17S, B18S and 32S aluminum alloys were twist bonded. These variations in the type of aluminum alloy appeared to have little influence upon the effectiveness of the bonding process by the twist method. Variations in bond strength were found from one type to another due to differences in strength of the aluminum alloy as annealed at 850°F. The majority of twist tests were conducted with AISI 303 stainless steel as the alloy bonded to the aluminum.

Hot-Press Bonding Results

Surface Finish: Surface preparations that were best for twist bonding, also worked equally well for hot press bonding. Several results are shown in table III. These tests showed again that the aluminum alloy should have a certain degree of roughness. The No. 50-grit belt grind was most effective. A polished surface was not necessary for the stainless steels, however, in contrast to twist bonding. A No. 240-grit belt grind followed by anodic etching in phosphoric acid gave excellent results. It was shown also that some preoxidation, up to at least 10 min at 850°F, could be tolerated without substantial lowering of bond strengths for 32S aluminum bonded to AISI 303 steel. This was evidenced in both peel and tensile tests.

Effect of Press Temperature Upon Bond Strength: Fig. 7 shows the effect of variations in bonding temperature upon bond strengths of hot-pressed samples of 32S alloy to AISI 303 and 321 steels. The required bonding temperature appeared to be an inverse function of pressure. The recommended range for hot-press bonding of 32S to AISI 321 steel was 750°-850°F. Bonding was done at lower temperatures but the bonds were unreliable, and high pressures were required.

Effect of Pressure Upon Hot-Pressed Bonds: Reference to fig. 7 shows also the minimum pressure required to produce satisfactory bonds between 32S aluminum and AISI 303 steel. Pressures of at least 10,000 psi were necessary at 850°F, 18,000 psi at 750°F, and 30,000 psi to 40,000 psi at 650°F, depending somewhat upon surface preparation. Pressures for bonding B18S alloy to AISI 303 steel were similar although no data are shown.

TABLE III

Effect of Surface Treatment Upon Hot-Pressed Bond Strengths of Several Aluminum-Steel Bimetals

Specimen No.	Aluminum	Steel	Tensile Bond Strength, PSI
1162, 1163	B18S, micropolish, ½ pct HF solution etch	AISI 303, No. 240 grit + H_3PO_4 anodic etch	500 (annealed)
999, 1000	B18S NaOH etch, HNO_3 solution etch	AISI 303, 3-0 emery + H_3PO_4 anodic etch	31,000–40,000 (annealed)
1144, 1145	B18S, No. 50-grit belt grind	AISI 303, No. 240 grit + H_3PO_4 anodic etch	31,500–50,000 (heatreated)
1160, 1161, 1158, 1159	32S, No. 50-grit belt grind	AISI 303, anodic etch	27,500–40,000 (heatreated)
896, 897, 898, 899	32S, No. 50-grit belt grind, NaOH, HNO_3, etch*	AISI 303, anodic etch	25,000–33,400 (heatreated)

* Samples 896–899 were preoxidized 10 minutes at 750°F–850°F before bonding. Solution treatment was at 950°F plus airblast quench, and 1.5 hrs age at 450°F.

Effect of Subsequent Heatreatment on Hot-Pressed Bonds: The beneficial effect of annealing at 850°F after bonding was quite apparent on hot-pressed samples, regardless of prior bonding temperatures (for 5-min bonding periods). Prolonged annealing at 850°F was not detrimental to bond strength. A photomicrograph of 32S aluminum bonded to AISI 303 steel after 60 hr at 850°F is shown in fig. 11.

Reference to table IV shows the optimum solution-treating temperature to be 920°F for bonded assemblies of B18S or 32S to AISI 303 steel. Temperatures of 950°F or higher caused marked lowering of bond strengths, as for twisted samples. The bond strengths obtained by solution-treatment at 920°F, airblast quenching and 450°F aging often approached the strength of the aluminum alloys proper (32S or B18S bonded to AISI 303). Considerable scatter in bond strengths was obtained, as shown in fig. 8, similar to twist-test results. The exact cause of the variations is unknown. Possible causes may include: slight variations in solution-treating temperatures, quenching practice, and size and shape of specimens.

Effect of Composition Upon Bond Strengths: Reference to table V shows bond strengths obtained for 32S and B18S alloys bonded to various steels. Bond strengths of a typical low-alloy steel (SAE 4340) to both 32S and B18S were equivalent to those of the aluminum alloy as annealed at 850°F. These combinations could be solution-treated and aged without considerable loss of bond strength.

Bond strengths of AISI 410 and 414 steels to 32S and B18S alloys were fairly high, particularly for the AISI 414 steel. If more specimens were tested, it is believed that both AISI 410 and 414 would give comparable average results. It should be noted that AISI 430 (high carbon, high chromium) steel did not give high bond strengths. It is suspected that the high carbon may have exerted some influence here. AISI 310 steel gave variable results, for unknown reasons. It is possible that the high nickel content (20 pct) may have been unfavorable, tending to form a nickel-aluminum phase during solution treatment at 920°F.

Peel tests run on several nickel-base alloys without solution-treatment showed that they likewise could be bonded by the hot-press process, although no quantitative measurements of bond strength were obtained. An attempt was made to improve the resistance of the bond to solution-treatment by means of various electroplated metals on the steel. Peel tests indicated that chromium was the only one of value. Several tests indicated that the bond of aluminum to chromium-flashed NE 8740 steel would withstand solution treatment at 930°F for several hours without deterioration.

A few tests run with X-750 alloys (Al, 6 pct Sn) indicated that this alloy could not be hot-press bonded to a low-alloy steel (NE 8740) under the conditions used.

Shear Test Results

Surface Finish: No attempts were made to vary the surface conditions from those previously found satisfactory on twist tests. The AMS 5700 valve-steel specimens were polished with 3-0 emery on the tapered surface and then anodically etched in phosphoric acid. The 18S aluminum-alloy specimens were macroetched in 20 pct sodium hydroxide followed by a bright dip in 50 pct nitric acid.

Effect of Temperature Upon Bond Strengths: Temperatures of 650° to 700°F gave the highest bond strengths, as shown in table VI. Temperatures above 700°F were not tried since this would have caused undesirable upsetting of the aluminum. It was desired to obtain a bonding process that could be used without confining dies.

Effect of Taper and Pressure: Tapers varying from 2° to 10° were tried and these showed no apparent correlation with bond strength (table VI). No actual pressures were estimated. The vertical downward travel of the bars into the aluminum was approximately 0.2 in.

Effect of Subsequent Heatreatment: All test specimens and results shown in table VI were in the annealed condition except as noted. Solution treatment at 920°F, airblast quench, and 450°F aging produced shear strengths of 13,000 to 15,000 psi, which were below those obtained for annealed specimens. It is not known whether the reduction in bond strength was caused by the geometry of the specimens as affected by quenching or by the composition of the alloys involved. AMS 5700 valve steel was not tested by the twist or hot-press methods previously described.

Variations in Composition: No steels other than AMS 5700 valve steel were tested. The shear-bonding method was used on both 18S and B18S aluminum alloys with equally good results in the annealed condition after bonding.

Discussion: This investigation has revealed several interesting features. Perhaps the most significant of these has been the beneficial effect of subsequent heatreatment upon bond strengths of aluminum-steel pressure welds. Such an effect has been observed for welds of other materials, although probably not to the same degree. The actual improvements in bond strengths as shown in this

TABLE IV

Effect of Solution-Treating Temperature Upon Bond Strengths of Aluminum Pressed to AISI 303 Stainless Steel at 850°F and 40,000 PSI

Specimen No.	Aluminum	Solution-Treating Temperature, °F	Tensile Bond Strength, PSI
1147, 1151	B18S	970	0
1149, 1166, 1167	32S	970	0–750
1028	B18S	960	5000
1029, 1030	32S	960	29,500–31,000
1031, 1032	B18S	950	10,100–18,500
898, 899	32S (preoxidized 10 min at 850°F)	950	25,000–33,000
1144, 1145, 1160, 1161	B18S	920	37,500–50,000
1158, 1159, 1165	32S	920	27,500–40,000

Note: Samples were held 2 hr at solution-treating temperature, airblast quenched and aged 1.5 hr at 450°F.

TABLE V

Effect of Variations in Composition Upon Bond Strengths of Aluminum Pressed to Steel at 850°F and 40,000 PSI

Sample No.	Aluminum Alloy	Steel	Condition	Tensile Bond Strength, PSI
1154, 1155	B18S	SAE 4340	annealed	34,000–35,500
1156, 1157	32S	SAE 4340	annealed	25,000–29,500
1037, 1038	B18S	AISI 410	heatreated	27,000–31,000
1124, 1125	B18S	AISI 414	heatreated	42,500–45,000
1039, 1040	B18S	AISI 430	heatreated	5000
1144, 1145, 1160, 1161	B18S	AISI 303	heatreated	31,500–50,000
1158, 1159, 1165	32S	AISI 303	heatreated	27,500–45,000
1111, 1112, 1035		AISI 321	heatreated	35,000
1036, 1059, 1060	32S	AISI 310	heatreated	0–31,000
1071, 1072	32S	AISI 310	heatreated	0,7500

Note: Annealing treatment consisted of 1.5 hr at 850°F and aircool. Solution treatment was 1.5 hr at 920°F, airblast quench and 1.5 hr age at 450°F.

investigation have been surprising. It is not known why bond strengths of the as-welded samples are increased so greatly by annealing. Some of the improvement is believed to be due to relief of residual stresses. This would be particularly true for twisted samples. However, the improvement is even greater for hot-pressed samples, and these probably do not contain as high a residual stress as welded (despite shear forces produced by breakdown of the high points on the roughened aluminum surface) since hot-press bonding at 750°F is above recrystallization temperatures for the aluminum alloys employed.

It is believed that most of the increase in bond strength is due to diffusion between the iron and aluminum. Such diffusion probably is aided by recrystallization. The lowest temperature at which such diffusion would occur is unknown, although improvement in bond strength of twisted 32S samples has been noted after 24 hr at 650°F. One theory suggests that the increase in bond strength may actually be due to formation of a very thin film of an additional phase, possibly $FeAl_3$ or Fe_2Al_7. If an effective film of this nature does exist, it cannot be observed by microexamination. If such a phase is thick enough to be observed microscopically, then the bond strength is greatly reduced.

The use of hot-press bonding with no external lateral movement is believed to be a new feature in the solid-phase welding of aluminum to steel. Methods developed heretofore have usually employed at least 5 pct deformation or more to achieve the shearing forces considered necessary for bonding. The absence of external movement makes the hot-press technique quite practical for any part adaptable to press forging. The hot-press method is believed to be restricted more to certain alloys than the twist process, due to the difference in required bonding temperature. It is conceivable that the twist process might be applied to bonding of certain copper and aluminum alloys.

The marked effect of a properly roughened aluminum surface on bonding is to be noted. Other investigators have emphasized cleanliness of surfaces to be pressure welded, but it is wondered whether surface roughness has been so well investigated. Wire brushing is often listed as one of the best surface preparations for various welding techniques, also for roll cladding. Little was done with wire brushing in this investigation, but limited tests indicate that it is at least as effective as macroetching. It might conceivably exert an effect similar to that shown by the No. 50-grit belt grind.

TABLE VI

Sheer-Bond Strengths of AMS 5700 Valve Steel Sheared Against 18S Alloy

Specimen No.	Taper	Bonding Temperature, °F	Shear Bond Strength, PSI
28, 29	2	550	85,000; 9000
10	2	650	22,500
11-1	4	650	17,500
11-2	6	650	17,500
11-3	8	650	17,000
8	10	650	23,500
37, 38	2	700	21,500; 20,000
13, 14*	2	650	13,200; 15,750

* All samples were annealed 1.5 hr at 850°F after bonding and aircooled, except for specimens 13 and 14, which were subsolution treated 1.5 hr at 920°F, airblast quenched, and aged 1.5 hr at 450°F.

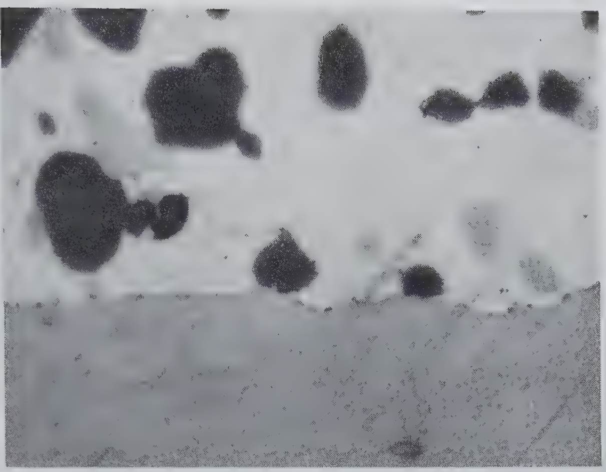


Fig. 11—Aluminum (32S) hot-press bonded to AISI 303 steel at 850° F, and annealed 60 hr at 850° F. Unetched. 2000 X.

A third feature which is felt to be unique is the ability of the hot-press method to bond aluminum to stainless steel despite the presence of controlled oxide films. This is somewhat contrary to established ideas on pressure welding. Kinzel, in his paper on solid phase bonding,[8] indicates that solubilities of oxides in the parent metals during subsequent annealing help to improve bonds in welds of ferrous materials, and the situation with aluminum alloys may be similar. The iron, nickel and chromium oxides may be soluble in the aluminum, or perhaps they are reduced with formation of aluminum oxide.

The fact that oxide films of limited thickness can be tolerated in these bonding processes adds greatly to their value for production purposes. Parts can be separately preheated prior to bonding, instead of heating up while under pressure in dies.

Summary: Three procedures for solid-phase bonding of aluminum alloys to various steels have been investigated and found capable of producing high bond strengths. The twist and shear methods are characterized by low bonding temperatures and considerable deformation. The hot-press method employs slightly higher temperatures and no external lateral movement. Variables investigated were bonding temperature, pressure, surface preparation, deformation, composition and subsequent heatreatment.

Regardless of initial bonding technique, strengths of as bonded assemblies were found to be increased as much as 100 pct by subsequent annealing. Both 32S and B18S alloys bonded to 18-8 stainless steel frequently could be strengthened by solution heatreatment and aging, without lowering of bond strengths

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[8] **"Solid Phase Welding," A. B. Kinzel. Welding Journal, Dec, 1944.**

Materials Handling

THE handling and transportation of materials in the foundry is a phase of the industry which has received too little attention until a very few years ago. The necessity for an efficient system of handling the materials which go into the product is extremely important because of the many tons of various materials which must be used in the manufacture of one ton of finished product.

The primary purpose of systematic handling is to serve production with the utmost efficiency. Next is to control handling costs, which of course includes safety in doing the job.

This paper will be presented before the Seventh Annual Electric Furnace Steel Conference, Dec. 8-10, Pittsburgh.

F. O. Lemmon is Melting Superintendent, Ohio Steel Foundry Co., Springfield, Ohio.

It became apparent to many foundry executives during periods of peak production such as were experienced during the war, that material-handling systems must be installed to make it possible to produce large tonnages of castings, and to maintain uniform flow from the scrap bin and storage shed to the shipping floor. Consequently, many elaborate mechanized methods were installed. These are still in use, and they make it possible to produce present peace-time tonnages much easier and cheaper than could have been done before. There is still plenty of room for improvement and in such a field of healthy competition as the foundry, it is wise to spend time, effort, and money to engineer and install systems of handling materials which will result in more efficient production methods and reduced costs.

In the writer's plant, the unloading of materials from railroad sidings has been one of many operations upon which great improvements have been made. Molding sand, for example, one of the chief raw materials of a foundry, has until a few years ago been unloaded by hand. Three or four men with wheelbarrows worked from the car to the bin, a distance of 100 ft or more. The operation required from half a day to a day per car. With the installation of an underground belt conveyor and elevator system, the bottom of a closed sand hopper can be opened allowing the sand to run through the grid onto the moving belt. The unloading of a 60 to 70-ton hopper now requires only periodic supervision and can be emptied in approximately 2 hr. In like manner, the method of unloading steel scrap has been changed from manual, which required two men about two days to shovel 50 tons, to the use of a yard crane and magnet, which transfers 50 tons from the car to the bin in 4 hr. Obviously but a relatively short time is required, what with the present price of labor to pay for mechanical unloading equipment through savings made.

The two materials mentioned above, although they comprise the bulk of the tonnage handled in the foundry, are not the only articles handled by methods which have been improved by study and engineering.

For materials such as furnace sand, iron ore, pig iron ferromanganese, ferrosilicon, ganister, limestone, bonding materials, electrodes, etc., special sheds are located adjacent to the railroad spur with the shed doors in line with car doors so that a roller conveyor can be utilized whenever possible. In the case of pig iron and iron ore, openings were cut in the roofs of the sheds so that the material can be unloaded with the magnet and the grab bucket from the cars through the roof. A special cover is then placed over the opening as a precaution against excess moisture.

Consider next the distribution of the material to the various production centers. All the distribution and transportation of materials in the writer's plant is under the supervision of the plant engineer. The cooperation of all departments in the plant is needed so that the system functions properly. There is a crew of yard men whose specific duty is to deliver materials to the various production units at certain times. It should not be necessary for highly skilled production men to transport materials or maneuver them into position so that they may be used. The cost is too great. Materials should be conveniently located in the production department and should be delivered by men trained in this type of work and whose job it is to transport and distribute the supplies. To make it possible for this to work, it is necessary to equip certain space with bins, boxes, etc., and keep it available for the placement of the materials to be used in the product. Management should take no chances with the backs, legs, and arms of the men who handle these materials. Whenever there is a need, a hoist specially designed for each article should be used.

Most of the hauling of materials from the storage sheds to the production departments is done with a tractor which pulls flat-bed trailers, skids, or side-dump trailers, according to the type of material being transported. For smaller loads, regular industrial lift trucks are used. An important factor from a maintenance cost angle, is to keep roadways in good repair so that rolling stock will not be shaken to pieces, and breakable materials will not be damaged.

The subject being considered certainly includes not only the handling of raw materials but also the

in the Foundry

by F. O. Lemmon

handling of processed materials which go into the manufacture of the product. The main ones are processed sand, refuse sand, molten metal, and rough castings. Some years ago in the Springfield plant, the old expensive and slow methods were replaced by mechanical means. The changes which have been made have all resulted in faster and more efficient distribution and better working conditions for the employees. For example, processed sand originally was exhausted from the mill into dump-bottom boxes which held about 1 ton of sand. These boxes were then hauled by overhead cranes to the bins at the molding machines. The sand then had to be shoveled into the flask by the molder. The installation of an overhead belt conveyor makes it possible to deliver sand to any molding unit almost continuously and allows the molder to fill his flask by opening the gate in the sand hopper which is directly over his machine. The use of this type of equipment results in the elimination of manpower at the sand mill and the crane, as well as lower costs in the actual molding of the job in the foundry. The same thing is true in the handling of used sand which is gathered under the shakeout machines in hoppers and carried in vibrator troughs onto underground asbestos conveyor belts and into the reclaiming system.

The carrying of molten metal in one-man monorail ladles to the molds to be poured is a great improvement over the old two-man shank system. Any foundry equipped with a mechanical conveyor system for delivering hot castings to the shakeout would be lost if it had to return to the old pan shakeout method. There is no doubt about these things all being the cause of increased production and higher efficiency in foundries today.

It is true that faster handling of materials can be accomplished by stimulating the labor with wage-incentive plans. Such plans have been installed in the Springfield plant for unloading certain materials from cars, milling of sand, pouring of molten metal, shakeout of castings, and the melting of metal. These systems have resulted in a reduction of manpower, lowering of manhours, and a reduction of delays as well as a higher morale of the workers.

The electric-furnace department is in a very good position to cut production costs by introducing proper methods of handling its materials. It seems there is always room for new ideas, no matter how many have been put into effect before. Certain methods in the Springfield melting department have resulted in more efficient operation. A top-charge furnace is used. It is charged with an orange-peel bottom bucket which receives its load while resting on the platform of a pit scale. The pit is of proper depth to allow the top of the charging bucket to be approximately level with the floor, thus providing a convenient method of filling the bucket.

Return heads and gates are hauled from the cleaning room in fabricated steel dump boxes which hold 2000 to 3000 lb. The scrap is dumped into the bucket by releasing the lock at the back of the box. No manual handling of the scrap is required by the furnace department. Plate scrap is previously brought from the outside storage bins in a large dump truck. Sufficient quantities of scrap can be stored inside the plant to last about ten operating days. It is piled close to the furnace department and the overhead crane uses a magnet to load the charging bucket from this source of supply. The second helper adds the required pig iron, necessary alloys, etc., thus completing the charge with a minimum of manual labor.

Other furnace supplies such as bottom sand, iron ore, pig iron, ferromanganese, ferrosilicon, electrodes, etc., are stored in sheds located outside, close to the furnace. These supplies are loaded by the second helper into boxes specially designed for hauling by the lift truck. For the materials used most, standby storage boxes are kept loaded and are held in the furnace department so that they can be readily substituted for the box just emptied. The additions of heated ferrochromium, which originally were made by shoveling, are now made by employing the use of a small brick-lined, fabricated bucket with a split bottom. The bottom is secured by a rope and when the furnace roof is removed, and the bucket lowered over the molten bath, the rope burns quickly, allowing the alloys to drop into the metal. This little idea has saved considerable time and energy.

The changes which have been made in the melting department have resulted in savings in a number of ways. First of all, the melting cycle for a 5-ton heat has been reduced from 120 min to 88 min, a saving of 26 pct. The manhours per melted ton have been reduced from 2.20 to 1.78, a saving of 19 pct. Many other advantages have resulted also, such as reduced labor manhours in the foundry and space is now available for the molders to place molds, which was not always the case before.

None of these improvements in methods are unique or secret. They are all well known to most foundry personnel. Some of them could have been instituted before they were, with very little expense involved, if the thought and planning had been started sooner. It is just necessary to look around with the thought in mind of saving time and money handling materials and there result any number of good ideas.

Electric Furnace Men Anticipate Record Attendance

(Continued from P. 19)

J. H. Kennedy, Supt. No. 1 Melter, Republic Steel Corp., Canton, Ohio.

d—Paddle and mixing ball.

Application of temperature measurements.

a—Relative cost of methods (radiation and immersion).

b—Accuracy.

(Preprinted) "Temperature Measurements in the Basic Electric Arc Furnace," by C. B. Post, Met., and D. G. Schoffstall, Melt Shop Met., Carpenter Steel Co., Reading, Pa.

D. G. Harris, Res., Republic Steel Corp., Massillon, Ohio.

G. E. Wagner, Melter Foreman, Electric Furnace Dept., Carnegie-Illinois Steel Corp., Duquesne, Pa.

J. G. Mravec, Melt Shop Met., Steel and Tube Div., Timken Roller Bearing Co., Canton, Ohio.

G. C. Olson, Mill Met., Atlas Steels, Ltd., Welland, Ont., Canada.

G. A. Lillieqvist, Res. Dir., American Steel Foundries, E. Chicago, Ind.

"Temperature Measurement and Temperature Control in Steel Foundries," by J. F. B. Jackson, Tech. Controller, David Brown and Sons, Ltd., Huddersfield, England.

Analysis measurements.

a—Spectrograph.

(Preprinted) "Melting Control with the Direct-Reading Spectrometer," by Earl Vance, Chief Chem., Timken Roller Bearing Co., Canton, Ohio.

P. R. Irish, Res. Engr., Bethlehem Steel Co., Bethlehem, Pa.

G. Nahstoll, Quality Control Lab., Ford Motor Co., Detroit.

"The Use of the Spectrograph in the Analysis of Special Steels," by M. L. Windle, Ch. Chemist, and W. H. Magrum, Simonds Saw and Steel Co., Lockport, N. Y.

C. B. Post, Met., Carpenter Steel Co., Reading, Pa.

A. C. Hale, Spectrographer, Copperweld Steel Co., Warren, Ohio.

E. O. Waltz, Ch. Chemist, Republic Steel Corp., Canton, Ohio.

b—Polarigraph.

W. C. McCrone, Supvr. Analytical Section, Chem. Dept., Armour Res. Foundation, Chicago.

Basic Steel Session

Friday, Dec. 9—9:30 a.m.-12:30 p.m., Urban Room.

Operating Improvements.

Factors to improve power consumption.

(Preprinted) R. M. Bayle, Consulting & Application Engr., Eng. & Svce. Div., Westinghouse Electric Corp., Chicago, Ill.

(Preprinted) L. A. Wynd, Supt. Electrical, Republic Steel Corp., Chicago, Ill.

Effect of large transformers on rate of production.

R. J. McCurdy, Supt. No. 2 Melt Shop, Republic Steel Corp., Chicago.

H. E. Phelps, Elec. Fce. Supt., Rotary Electric Steel Co., Detroit.

W. M. Patterson, Electric Fce. Supt., Allegheny-Ludlum Steel Corp.

S. Myford, Melter, Copperweld Steel Corp., Warren, Ohio.

Method to improve electrode quality and lower electrode consumption.

"Good Joint Making Practice," by W. H. Herbert, Head, Tech. Dept., Great Lakes Electrode Co.

"Improved Methods for Handling and Shipping Graphite Electrodes," by John A. Shaw, Tech. Adv., International Graphite and Electrode Corp.

"Graphite Electrodes in Electric Furnace Operations," by H. G. MacPherson, National Carbon Co.

"Tightening Electrodes," by J. H. Eisaman, Supt. No. 2 Electric Fce. Shop, Carnegie-Illinois Steel Corp., Chicago.

"Automatic Electrode Slipping," by S. Myford, Melter, Copperweld Steel Corp., Warren, Ohio.

Deoxidation practice on rimmed and semi-killed steels.

C. F. Staley, Supt. Electric Steel Melting Dept., Armco Steel Corp., Middletown, Ohio.

J. W. Kinnear, Jr., President, Firth-Sterling Steel & Carbide Corp., McKeesport, Pa.

C. H. Weimer, Mill Met., Copperweld Steel Corp., Warren, Ohio.

Keith Moore, O. H. & Electric Fce. Supt., Steel Co. of Canada, Ltd., Hamilton, Ontario, Canada.

J. Atkinson, O. H. Supt., Dominion Foundries and Steel, Ltd., Hamilton, Ont., Canada.

Acid Technical Session

Friday, Dec. 9—9:30 a.m.-12:30 p.m., Monongahela Room

Use of Oxygen in Electric Furnace Melting.

Oxygen in steelmaking.

(Preprinted) "Investigation of Five Ton Acid Electric Steel Practice to Determine a Control of Metallurgical Factors Influencing the Quality of Oxygen Decarbonized Heats," by Charles A. Faist, Res. Member and Clyde Wyman, Chief Met., Burnside Steel Foundry Co., Chicago.

C. C. Spencer, Melt. Supt., Electric Steel Castings Co., Indianapolis.

John W. Juppenlatz, Chief Met., Lebanon Steel Foundry Co., Lebanon, Pa.

C. J. Jernstrom, V.P., Cooper Alloy Foundry Co., Arlington, N. J.

W. T. Bryan, Met, Duriron Co., Inc., Dayton.

J. B. LaPota and Lee H. DeWald, Metallurgists, Res. & Dev. Dept., National Cylinder Gas Co., Chicago.

Manufacture of high-chromium steel in the acid arc furnace.

(Preprinted) D. C. Hilty, Met. Res. Engr., Union Carbide & Carbon Res. Labs., Niagara Falls.

Basic Technical Session

Friday, Dec. 9—2:00-5:00 p.m., Urban Room

Electric Furnace Refractories.

Sillimanite roof refractories.

R. E. Wolfensperger, Refractory Engineer, Bethlehem Steel Co., Bethlehem, Pa.

Evaluation of refractories.

John Topping, Ceramic Engr., Carnegie-Illinois Steel Corp.

Palletizing of refractories.

Motion Picture and W. G. Nichol, Mgr., Methods Engrg. Bureau, Carnegie-Illinois Steel Corp., Pittsburgh, Pa.

Electric furnace bottom and pouring refractories.

M. Fedock, Ceramatist, Republic Steel Corp., Canton, Ohio.

L. L. Wells, Jr., Supvr. of Ceramics, S. Works, Carnegie-Illinois Steel Corp.

Production of sea water magnesite.

O. M. Wicken, Supt., Northwest Magnesite Co., Cape May, N. J.

Acid Technical Session

Friday, Dec. 9—2:00-5:00 p.m., Monongahela Room

Gases Other Than Oxygen in Steel.

Effect of furnace practice on the hydrogen content of steel.

(Preprinted) Sam F. Carter, Jr., Asst. Melt. Supt., American Cast Iron Pipe Co., Birmingham, Ala.

Flushing hydrogen from molten steel with neutral gases.

C. E. Sims, Asst. Dir., Battelle Memorial Inst., Columbus, Ohio.

C. SHELDON ROBERTS

aime NEWS

Mining Division Established at Sept. Board Meeting

Recognition of the Mining, Geology, and Geophysics Division of the AIME was accorded by the Board of Directors at their meeting on Sept. 27 at Columbus, Ohio. Some changes in the proposed bylaws of the new Division were believed desirable by the Board, and a committee consisting of Philip Kraft, chairman, with A. B. Kinzel and Donald H. McLaughlin, was appointed to work with the proposed executive committee of the new Division to draw up bylaws that would be acceptable to all the groups involved and to the Board. Temporarily, and pending acceptance of any revisions found necessary in the bylaws, Philip J. Shenon will act as Chairman of the new Division, and James K. Richardson, Secretary. They will also be Chairman and Secretary, respectively, of the Geology group in the new Division. Other members of the temporary Executive Committee of the Division are: J. Murray Riddell and O. A. Rockwell, Chairman and Secretary respectively of the mining group, and James B. Macelwane and Sherwin F. Kelly, Chairman and Secretary respectively of the geophysics group. Sub-committees will be appointed to permit the important work of the new Division to go forward until the time of the next Annual Meeting, or until a permanent organization is set up and approved by the Board. Among the important duties demanding immediate attention is the securing of papers for the Annual Meeting program and their review for acceptance for publication.

J. L. Gillson, chairman of the Special Committee on Democratization (E. A. Anderson and George B. Corless being the other members), made a report recommending formal organization of the "Council of Section Delegates" in line with the suggestions of the Johnson Committee, and offered provisional bylaws which would permit the Council to function at the forthcoming Annual Meeting. The Council would consist of a delegate from each Local Section, with traveling expenses paid to the Annual Meeting, each delegate normally serving for two years. For the first year, half of the Local Sections would elect a delegate for a one-year term, and half for two years; thereafter, half of the Sections would elect a delegate every year for a two-year term. This would assure that at least half of the delegates would have at least a year's experience. They would elect their own officers and prepare their own agenda, probably meeting at least a day before the Board meets so that any resolutions might be brought before the Board.

Announcement was made of the personnel of the Technical Publications Committees (which recommend acceptance or rejection of papers for publication) for the year beginning Oct. 15, 1949:

AIME: E. C. Meagher, chairman; Anthony Anable and Francis B. Foley, vice-chairmen; E. J. Kennedy, Jr., secretary; Robert H. Aborn, Vinton H. Clarke, Charles W. Eichrodt, Kenneth E. Hill, Paul F. Kerr, Charles H. Lambur, J. I. Laudermilk, W. H. Loerpabel, Earl W. Palmer, L. C. Raymond, J. E. Smart, Jr., Felix E. Wormser.

Auxiliary Publications Committees:

Coal Division: H. P. Greenwald, chairman; David H. Davis, Carroll F. Hardy, Raymond C. Johnson, H. J. Rose, G. A. Shoemaker, J. A. Younkins, Jr.

Extractive Metallurgy Division: Philip T. Stroup, chairman; Matthew A. Hunter, John D. Sullivan.

Industrial Minerals Division: H. D. Keiser, Chairman; Oliver Bowles, Oliver C. Ralston, Howard I. Smith, Richard W. Smith.

Institute of Metals Division: O. B. J. Fraser, chairman; W. C. Ellis, W. D. France, W. R. Hibbard, Jr., E. H. Hollingsworth, R. L. Rickett, R. P. Seelig, Ralph W. E. Leiter.

Iron and Steel Division: M. Tenenbaum, chairman; A. G. Forrest, B. R. Queneau, C. S. Smith, J. M. Stapleton, F. M. Washburn, Otto Zmeskal.

Minerals Beneficiation Division: M. D. Hassialis, chairman; S. R. B. Cooke, F. M. Lewis, S. D. Michaelson, H. Rush Spedden.

Mineral Economics Division: Charles H. Behre, Jr., chairman; Clayton G. Ball, Kenneth E. Hill, G. W. Josephson, Samuel G. Lasky.

Mineral Industry Education Division: Charles H. Behre, Jr., chairman; Thomas L. Joseph, William B. Plank, H. H. Power, A. W. Schlechten.

Petroleum Division: O. F. Thornton, chairman; J. M. Bugbee, vice-chairman; R. C. Craze, E. N. Dunlap, J. L. Hoyt, Jr., D. L. Marshall.

The secretary announced that no supplemental names had been received for nominations for Institute and Divisional officers for 1950 so that no letter ballot would be necessary.

A petition to organize a new Local Section of the Institute, composed of members working in the Florida phosphate industry, was approved by the Board. It will be known as the Florida Section, and would embrace the entire state, if this is agreeable to the petitioners.

Recommendations of appropriate committees for the award of Institute Medals at the forthcoming Annual Meeting were approved as follows:

Saunders Mining Medal to H. N. Eavenson.
Douglas Metallurgical Medal to Francis C. Frary.
Lucas Petroleum Medal to William E. Wrather.
Erskine Ramsay Coal Medal to Paul Weir.
Robert H. Richards Award to Arthur F. Taggart.
R. W. Hunt Award (silver medal) to J. S. Marsh.

J. B. Vilella has been selected as the Howe Memorial Lecturer for 1951.

THE DRIFT OF THINGS

. . . as followed by EDWARD H. ROBIE

Divisionalization Completed

Another of the major recommendations of the Johnson Committee, whose report was accepted by the AIME Board of Directors at the Annual Meeting last year, was finally brought to complete fruition at the September Board meeting. The Mining, Geology, and Geophysics Division was formally recognized, the last of the ten projected Divisions of the Institute. Practically every member should now find one Division to represent his technical interests, and many members whose interests are somewhat wider than usual will find it desirable to belong to more than one division. No fees for Divisional membership are assessed; membership merely puts one on the list to receive all announcements of Divisional meetings, permits one to vote for Divisional officers, and lists a member as available for Divisional committee work. A canvass is being made this fall to determine the Divisional affiliation of every Institute member, which will supersede all previous incomplete canvasses that have been made. This is not intended to change in any way the present selection of journals.

The Mining, Geology, and Geophysics Division, with the Minerals Beneficiation Division, the Coal Division, and the Industrial Minerals Division (Non-metallics) comprise the Mining Branch; the Extractive Metallurgy Division, the Institute of Metals Division, and the Iron and Steel Division comprise the Metals Branch; and the Petroleum Division is the only component of the Petroleum Branch, the Petroleum Branch and the Petroleum Division thus being synonymous. "Mining Engineering" contains all the papers published by the Mining Branch; the "Journal of Metals" all those of the Metals Branch; and the "Journal of Petroleum Technology" all those of the Petroleum Branch.

Two other Divisions complete the ten: the Mineral Economics Division and the Mineral Industry Education Division. The papers of these Divisions may appear in any one of the three journals, if of particular interest to the particular readership; or, if thought of interest to all members, may be included in the AIME News section.

Bylaws of the new Division were tentatively drawn up but several of the directors present at the September meeting believed they might be capable of improvement so their final acceptance was postponed, a committee being appointed to review them. However, a temporary executive committee representing metal mine operating men, mining geologists, and geophysicists, was appointed to act until all details have been worked out to the satisfaction of all concerned. This committee, of which Philip Shenon is chairman, with the aid of subcommittees, will solicit papers and prepare the program for the Division's sessions at the Annual Meeting in February, and will make recommendations to the Institute's Technical Publications Committee as to publication of papers in its field. Inasmuch as geophysics is not within the present interests of the Petroleum Branch, all geophysicists who are members of the Institute will presumably have their primary interest in this new Division.

The bylaws of the Institute provide that each of the three Branches have a governing council, which shall include one member from each of the Mineral Economics and the Mineral Industry Education Divisions, as well as at least one member from each of the constituent Divisions; further that council membership shall be equally divided between the constituent Divisions. No council has yet been set up for the Mining Branch, but it would have a minimum of six members, according to the bylaws, or it might have ten members, if each of its Divisions had two representatives instead of one. The Metals Branch Council must have a minimum of eight members, which it now has, consisting of A. A. Smith, Jr., chairman; Ernest Kirkendall, secretary; and D. S. Eppelsheimer, C. D. King, C. C. Long, F. N. Rhines, Gilbert Soler, and J. D. Sullivan. The Petroleum Branch council is required to have a minimum of six members, but currently has ten, or eleven if the Treasurer be included. This council is synonymous with the officers of the Petroleum Division.

National and Divisional Meetings

When the Institute had all of its Annual Meetings in New York, and few Divisional meetings, it was customary to have at least one Institute meeting each year in another part of the country, usually in the fall, which became known as a Regional Meeting, or, more recently, the Mid-Year Meeting.

Some, at least, of the reasons for these mid-year meetings have now ceased to exist. The experiment of having occasional Annual Meetings outside of New York has proved successful, with the 1946 meeting in Chicago and the 1949 meeting in San Francisco; the 1951 Annual Meeting is scheduled for St. Louis, and the 1953 meeting may be held in Los Angeles. Thus members in North America, no matter where they live are not too far away from at least an occasional Annual Meeting. Another reason why all-Institute mid-year meetings are no longer so necessary is the desire of the various Divisions of the Institute to have their own meetings. The Petroleum Branch thus has the established practice of having one meeting in the fall of each year in the Mid-Continent or Gulf Coast areas and one in southern California. The Institute of Metals Division customarily meets at the same time and place as the American Society for Metals, during the National Metal Congress, and also in the spring at an Eastern city. The Iron and Steel Division, through its Blast Furnace and Raw Materials, Open Hearth, and Electric Furnace Committees, has several national and regional meetings in the course of a year. The Coal Division for years has united with the Fuels Division of the American Society of Mechanical Engineers in a Fuels Conference in the fall. The Industrial Minerals Division has customarily held an Eastern and Western meeting of its own each year, this year three such meetings being scheduled—at Tampa, Golden, and Los Angeles.

No fall meeting being scheduled for 1950, two other Divisions are contemplating meetings a year hence: The Minerals Beneficiation Division at Duluth, and the Mineral Economics Division at Washington. Conceivably the new Mining, Geology, and Geophysics Division or the Iron and Steel Division might wish to participate at Duluth.

Whether or not the usual fall meeting of the Institute should now be discontinued is therefore something to consider, and the opinions of members will be welcomed. Even should they be discontinued as annual fixtures, an occasional special meeting of the Institute might be held in the summer or fall.

The Secretary Goes Afield

Progress in reorganization having reached a point where continuous duty in New York did not seem quite so necessary, and where some first-hand reactions of the membership to what has been done seemed desirable, we set out in the family Ford on Sept. 22 to take the issues to the voters.

Our first business stop was Columbus, Ohio, for the Mid-year meeting. From the standpoint of the variety and number of technical papers presented this was perhaps the most successful fall meeting the Institute has ever staged. The local committee worked hard and successfully to assure a smooth-running meeting in every respect.

After leaving Columbus we enjoyed a luncheon meeting with Art Focke and a group of AIME members in Indianapolis; an early meeting there is planned. Art is a loyal Institute member as well as the president elect of the ASM. Next day we had a luncheon meeting with the officers of the St. Louis Section, and talked over plans for the Annual Meeting in that city in 1951.

That same night we arrived at Rolla, Mo., where we had a dinner meeting with some of the faculty and students and their wives, followed by a meeting of the Student Chapter. The mining school at Rolla now boasts of more than 500 students, has many distinguished graduates, and promises to extend the relative number of its graduates in the world's mining camps. The next day was Sunday, but that did not prevent the officers of the Tri-State Section from gathering with us at the home of its Secretary, J. C. Stipe, in Baxter Springs, and listening to the World's Series game. We managed to work in mention of AIME affairs during the commercials.

Then on to Muskogee for the night and more than 400 miles through rain the next day to Austin, where we arrived just in time to give a talk before the petroleum engineering students. On the way we had lunch with the Petroleum Branch staff at Dallas, with the exception of Bill Strang, who had gone on to San Antonio to prepare for the fall meeting of the Branch. Even with Bill absent, we can assure all AIME members visiting in Dallas, whether petroleum men or not, that they will enjoy meeting Joe Alford, editor of JPT, and his capable assistant, Mrs. Haywood; and should not miss the smiles and eye twinkles of Peggy Hardy.

In past years we have heard of the great success of the fall petroleum meetings but we have never had the privilege of attending one since we took our first airplane ride in a Ford tri-motor plane to the Ponca City meeting some fifteen years ago. At least 1200 people attended the San Antonio meeting; almost exactly 900 men were registered, and at least 300 ladies were present. We were enormously impressed with the technical program, which was mostly over our head, but which quite evidently had many important papers on concurrent sessions for three days; with the type and number of the people present; with San Antonio as a locale for the meeting; and with the social features. One cannot but notice that Petroleum Branch members are relatively young men—few gray hairs and bald heads were evident—and that they bring to the meetings and to the Institute all the enthusiasm of virile youth. The Branch has been particularly successful since the Dallas office was established, and a similar field office for the Mining Branch in Utah or Colorado seems indicated. At the dinner dance at the Seven Oaks Club, a most attractive spot a few miles north of the city, 860 persons were served under ideal conditions. As a special feature the Texas boys staged a full eclipse of the moon, which took place entirely within the time the group was partaking of the al fresco dinner. It must be admitted, however, that the Mexican singers and dancers attracted greater interest.

Following San Antonio, our next stop was Carlsbad, where we had a luncheon meeting with the officers of the Carlsbad Potash Section. This local group, representing but one industry in a closely limited area, has had most successful monthly meetings, and has done much in increasing co-operation among the three companies that are operating in the area. From there we dropped down to El Paso in the afternoon and next morning went up on the hill to talk to the students at Texas Western College. Gene Thomas, John Graham, and Guy Ingersoll seem to be doing a fine job here in turning out mining engineers. A luncheon meeting with the officers of the El Paso Metals Section at the del Norte followed, with Ed. Tittman presiding. No doubt we should admit that we did get in a bit of recreation at Juarez the night before. We can recommend the Charmant as a place to dine, and if one does not have the opportunity to visit the Carlsbad cavern, the Cave of Music is a reasonable artificial facsimile of a small part thereof. The only disappointing feature of our trip to Juarez was our neglect of the opportunity to buy the allowed gallon of liquor, which can be obtained for about one-third of the U. S. price, or about $1 for Bacardi rum.

Personals

Richard C. Anderson completed his course in mining engineering at the New Mexico School of Mines last July and is employed by the Allis-Chalmers Mfg. Co. His new address is 1021 N. 39th St., Milwaukee 8, Wis.

T. J. Ballard has resigned from the Bureau of Mines to take the post of general manager of the Dunbar Corp., Dunbar, Pa. This Corporation has extensive coal and silica sand deposits, owns the New Haven and Dunbar Railroad and produces a high quality glass sand for various glass plants of the region.

A. T. Barr has been promoted from mine superintendent to general superintendent of the New Cornelia copper mining branch of the Phelps Dodge Corp. at Ajo, Ariz.

James A. Barr, Sr., retired as chief engineer of the International Minerals and Chemical Corp., Chicago, after 38 years of service, and then was appointed consulting engineer for the concern. He has opened an office as a consulting engineer specializing in nonmetallics and can be reached at his home at 505 Haylong Ave., Mt. Pleasant, Tenn.

A. H. Barrios, recent Mackay School of Mines graduate, is employed by the Anaconda Copper Mining Co. and is taking their special training course for junior engineers. His address in Butte is 733 W. Park St.

Robert R. Bergis resigned as salesman for the Atlas Powder Co. in August and is now associated with the Industrial Supply Co. in Roseburg, Oreg.

M. John Bernstein has returned to the Colorado School of Mines to study for his master's degree in mining.

C. A. Botsford left New York on Sept. 28 for Siam and Burma as a consultant for New York industrialists interested in tin, tungsten, and lead mining. He returned to the States last May after 27 months as chief of the minerals branch, mining and geology division, Natural Resources Section of General MacArthur's headquarters in Tokyo.

Alan T. Broderick has gone to Kellogg, Idaho, as a geologist with the Bunker Hill & Sullivan Mining and Concentrating Co.

John G. Broughton has been made New York State geologist. He had been assistant state geologist.

Brinton C. Brown is a mining engineer with the Bureau of Mines at the experimental oil shale mine, Rifle, Colo.

Leroy T. Brown has been working for the W. H. Loomis Talc Corp. since last spring. His address is P. O. Box 267, Gouverneur, N. Y.

H. M. Corley

H. M. Corley has been appointed manager of the chemical division of Armour & Co. He joined the Company in 1927 with most of his work devoted to the development of new chemicals, commercial processes for manufacturing them, and new products in which these new chemicals could be used. He is responsible for chemical plant management and operation, chemical sales, market development and market research on new items.

Arno C. Fieldner

Arno C. Fieldner, chief of the fuels and explosives division of the Bureau of Mines, was honored with the distinguished service award and gold medal by the Department of the Interior in recognition of his notable contributions to fuel technology during forty years of service.

Donald F. Campbell has changed his address from Rio de Janeiro, Brazil, to care of Geophoto Services, 305 Ernest & Cranmer Bldg., Denver 2, Colo.

James B. Chaney is with the Baroid Sales Division, National Lead Co., Box 218, Potosi, Mo.

Denton W. Carlson has had a memorable year; he got his B.S. in mining engineering from Stanford, was married on June 20, honeymooned through several Western States, and was employed by the Anaconda Copper Mining Co. on a two year training program.

Glenville A. Collins returned to his offices in Santa Barbara, Calif., after a busy summer examining uranium properties in Canada.

H. R. Cooke, Jr., formerly with the Chile Exploration Co. in Chuquicamata, has gone to Llallagua, Bolivia, to work for Patino Mines & Enterprises Consolidated.

Francis X. Corbett is in Georgetown, Colo., working for Gold Mines Consolidated, Inc., in the capacity of operating engineer.

William J. Coulter has been made a vice-president in charge of mining operations for the Climax Molybdenum Co. With the Company since 1927, he has been manager of mining operations since 1934.

K. N. Das has been touring the States studying field problems in mining and engineering geology, ground water and soil conservation methods as part of a MIT practical program. He has gone to England and Europe now for observational studies on reclamation problems.

David B. Dill, Jr., is in Monterrey, Mexico, with Cia. Minera de Penoles.

James S. Dodge, Jr., employed by the Natural Resources Section, GHQ, SCAP, Tokyo, Japan, since September, 1946, has resigned as deputy chief, mining and geology division, following completion of a draft for the report "Manganese Resources of Japan" to take graduate studies in economic geology at Stanford University beginning the fall quarter.

C. P. Donohoe has gone to Cananea, Mexico, as general superintendent of the Cananea Consolidated Copper Co.

A. Emond is in San Felix, Edo. Bolivar, Venezuela, on a two year contract with the Iron Mines Co. of Venezuela, a subsidiary of the Bethlehem Steel Corp.

Frank M. Estes has returned to the States from Colombia where he spent the last seventeen years. His present address is 208 E. Cherry Circle, Memphis, Tenn.

Louis W. Ferguson is temporarily attached to the Economic Co-operation Administration and can be reached at the Strategic Materials Division, 800 Connecticut Ave., Washington 25, D. C.

P. V. G. Ford has been appointed assistant general manager of the Sinai Mining Co., Abu Zenima, care Port Said and Suez Coal Co., Port Twefik, Egypt.

R. E. Froiseth, after spending 2½ years as project manager for Drake-Puget Sound Contractors on Naval construction in the Aleutian Islands, has decided to take a long rest and absorb some California sunshine. His address is in care of N. W. Howard, 521 Toro Canyon, Santa Barbara, Calif.

Daniel Geary has enrolled at the Montana School of Mines to complete work for a degree. His address is 1421 W. Porphyry, 413 Mines Vets Homes, Butte.

Latham B. Gray, Jr., has finished his studies at the Michigan College of Mining and Technology, receiving a B.S. degree in mining engineering. He is employed by the Bethlehem Collieries Corp., subsidiary of Bethlehem Steel, at Idamay, W. Va.

K. B. Gross, formerly with the New Guinea Goldfields, Ltd., has accepted an appointment as assistant general manager of Mount Isa Mines, Ltd., Mount Isa, Queensland, Australia.

W. J. Guay has changed his address from the Howe Sound Mining Co., Holden, Wash., to Apt. 4, 826 E. Center St., Pocatello, Idaho. He is now employed by the Westvaco chemical division of the Food Machinery and Chemical Corp.

Graham Hall, who is assistant superintendent and chief geologist of Electrolytic Zinc Co. of Australasia, Ltd., west coast department, at Rosebery, Tasmania, visited various mining centers in the United States and Canada during July, August and September.

John R. Hallock, a Colorado School of Mines man, is working for the Idarado Mining Co. at Ouray, Colo.

J. L. Hamilton has severed relations with the Republic Steel Corp. and is now employed by the Island Creek Coal Co., Pond Creek Pocahontas Co., and Marianna Smokeless Coal Co. as vice-president in charge of operations.

Robert L. Hamilton has the job of hydraulic engineer with the International Boundary and Water Commission, Alpine, Texas, working on field measurement of water flow.

R. S. Handy, formerly mill superintendent for the Bunker Hill & Sullivan Mining & Concentrating Co., Kellogg, Idaho, has retired as consulting metallurgical engineer for the company and he and Mrs. Handy have moved to 2329 Humboldt St., Santa Rosa, Calif., where he intends to try his hand at flower gardening.

James Gibson

James Gibson, who has been employed for the past five years in placer examinations for the American Smelting and Refining Co., has left AS&R to engage in placer mining in Peru. His present address is Quincemil, via Cuzco, Peru.

Tommy Martin

Tommy Martin, head of the French Advisory Mission at Camp Sherman, Chillicothe, Ohio, in 1917 and 1918, now a consulting engineer, can be reached in Megrine, Tunisia.

J. D. Harlan, since resigning as a vice-president of U. S. Smelting Refining and Mining Co., although not out after professional work, has undertaken some special tasks, including two trips to France and Maroc, and one to Berlin and the Ruhr industrial district. In June he completed a mining engineering assignment at the Hazleton shaft of the Lehigh Valley Coal Co. and in September was at Wilkes-Barre, Pa., on similar work. His permanent home address is still 2017 5th Ave. N., Seattle 9.

Donald F. Haskell can be reached at the Benguet Consolidated Mining Co., Baguio, Philippine Islands.

Earl F. Hastings has been appointed director of the securities and investments division of the Arizona Corporation Commission. In accepting this appointment he resigned as secretary-treasurer of the Western Perlite Corp. and dropped his mining and metallurgical consulting practice.

Arthur W. Heuck can be reached now in care of Cyprus Mines Corp., Skouriotissa, Nicosia, Cyprus.

Warren H. Hinks, Jr., since his graduation in June from Penn State, has been employed as a mucker by the U. S. Smelting Refining and Mining Co. at their Lark mine.

Francis G. Hoffman is working for the Homestake Mining Co., Lead, S. Dak., as a mine surveyor. His home address in Lead is 214½ Arlington St.

Edward Holloway, surviving partner of Douglas, Armitage & Holloway, has formed a partnership for the general practice of law with members of the firm of Bannister, Stitt & Krause, under the firm name of Bannister, Stitt, Holloway & Krause with offices at 40 W. 40th St., New York 18.

R. C. Howard-Goldsmith is now employed as a mine foreman by the Cerro de Pasco Copper Corp., Cerro de Pasco, Peru.

Charles D. Hoyt, having received one of the Fulbright Scholarships that are offered by our Government to graduate students in foreign countries, has gone to the Institute of Technology at Trondheim. He plans to spend the year observing the various phases of Norway's mining industry.

Hsi Keng Hu is employed as assistant mill superintendent by Cia. American Smelting Boliviana, a subsidiary of American Smelting and Refining, and is addressed in care of the Company, Casilla 901, La Paz, Bolivia.

Paul W. Hughes has changed his address from the Dept. of Geology, University of Arizona, Tucson, to the Museum of Northern Arizona, Flagstaff.

Gordon E. Irving is ore testing engineer for the Allis-Chalmers Mfg. Co., West Allis, Wis.

Lytton Francis Ivanhoe, Jr., who received his B.S. degree in mining in

1942 from the South Dakota School of Mines, and who has been attending Stanford University, has recently been employed as mining engineer by the Standard Oil Co. of California in the exploration department, 11-C Camp, Taft, Calif.

Gunnar S. Johnson, general manager of the East Chicago, Ind., plant of the Eagle-Picher Co., retired from active duty on Aug. 1 When Eagle-Picher purchased this plant in 1946, he was granted a leave of absence from Anaconda to assist in the initial operations. Mr. Johnson leaves the East Chicago plant after 31 years of active duties in capacities from research chemist to general manager. He plans to retire to his farm in the Catskills and to spend part of the time with his family in Florida.

J. D. McClintock

J. D. McClintock recently returned to the States from an assignment with the United States Philippine War Damage Commission. He was in charge of appraisal and allocation of payments to mining operations in the Islands.

Roy Johnson on July 1 was appointed manager of the central industrial division of The Dorr Co., with headquarters in Chicago. **H. W. Hitzrot,** of New York, previously handled this territory of the industrial division in addition to his regular duties as manager of the eastern industrial division.

Robert W. Johnson, formerly of Lead, S. Dak., can be reached in care of the Braden Copper Co., Rancagua, Chile.

Vard H. Johnson, of the U. S. Geological Survey, has started an investigation of the coking coal and geological

Coming Meetings

NOVEMBER

1 Society for Applied Spectroscopy, New York City.
1-5 Pacific Chemical Exposition, California Section, American Chemical Society, San Francisco Civic Auditorium.
2 Chicago Section, AIME. Ladies Night. J. P. Skinner on "Synthetic Sapphire."
2-4 American Society of Civil Engineers, fall meeting, Washington.
4 Columbia Section, AIME.
7 Boston Section, AIME.
7-10 AIChE, annual meeting, Pittsburgh, Pa.
7-12 International congress on tunnel driving in rock formation, organized by the Societe de l'Industrie Minerale. Information on meeting available from French Mining Mission, 1322 18th St., N. W., Washington, D. C.
8 Delta Section, AIME. Problems of offshore drilling.
8 East Texas Section, AIME.
8-11 Industrial Minerals Division, AIME, Tampa, Fla.
9 El Paso Metals Section, AIME.
9 San Francisco Section, AIME.
9 New York Section, AIME. Ladies Night. C. Goodman on "Atomic Energy."
10-11 National Air Pollution Symposium, Huntington Hotel, Pasadena, Calif.
10-14 ASTM, first Pacific area national meeting, San Francisco, Calif.
11-12 Central Appalachian Section, AIME., and W. Va. Coal Mining Inst., Summit Hotel, Uniontown, Pa.
11 Rio de Janeiro Section, AIME.
12-14 Geological Society of America, annual meeting, Hotel Cortez, El Paso.
14 Arizona Section, AIME, annual meeting, Pioneer Hotel, Tucson.
15 Gulf Coast Section, AIME.
15 Washington, D. C., Section, AIME.
16 Southwest Texas Section, AIME.
16-18 Industrial Hygiene Foundation, 14th annual meeting, Mellon Institute, Pittsburgh.
16-18 Geological Society of America, annual meeting, Hotel Statler, Washington, D. C.
17 Carlsbad Potash Section, AIME.
17 Utah Section, AIME.
18 Oregon Section, AIME.
18 St. Louis Section, AIME, joint meeting with Woman's Auxiliary.
21 Detroit Section AIME.
22 Montana Section, AIME.
26 Wyoming Section, AIME, fall meeting, Townsend Hotel, Casper.
27-Dec. 2 ASME annual meeting, Statler Hotel, N. Y. C.
28 Alaska Section, AIME.
28-Dec. 3 22nd Exposition of Chemical Industries, New York City.

DECEMBER

2 Columbia Section, AIME.
4-7 AIChE, national meeting, Pittsburgh, Pa.
5 Boston Section, AIME.
6 Society for Applied Spectroscopy, New York City.
7 American Mining Congress, Annual Business Meeting, New York City.
7-9 Eighth Annual Conference, Electric Furnace Steel Committee, Iron and Steel Division, AIME, Hotel William Penn, Pittsburgh.
7 Chicago Section, AIME. W. C. Schroeder on synthetic liquid fuels.
7 New York Section, AIME. L. E. Young on research in coal mining.
8-10 Seventh Annual Conference, Electric Furnace Steel Committee, Iron and Steel Division, AIME, Hotel William Penn, Pittsburgh.
9 Rio de Janeiro Section, AIME.
9 St. Louis Section, AIME, York Hotel.
13 Delta Section, AIME. W. H. Skinner on gas condensate well corrosion problems.
13 East Texas Section, AIME.
14 Connecticut Section, AIME. F. H. Wilson on intergranular parting of 70:30 brass.
14 El Paso Metals Section, AIME.
14 San Francisco Section, AIME.
15 Carlsbad Potash Section, AIME.
15 Utah Section, AIME.
16 Oregon Section, AIME.
26-31 AAAS, Penn zone hotels and Columbia Univ., New York City.

JANUARY 1950

18-20 American Society of Civil Engineers, annual meeting, New York.
30-Feb. 3 AIEE, winter meeting, Hotel Statler, New York.

FEBRUARY 1950

10 Southwestern Section, Open Hearth Steel Committee, Iron and Steel Division, St. Louis, Mo.
12-16 Annual Meeting, AIME, Statler Hotel, New York City.

APRIL 1950

4-7 Nat'l Assn. of Corrosion Engineers, St. Louis.
10-12 Open Hearth Conference, and Blast Furnace, Coke Oven and Raw Materials Conference, Netherlands Plaza Hotel, Cincinnati.
19-21 American Society of Civil Engineers, spring meeting, Los Angeles.
23-26 American Ceramic Society, annual meeting, New York City.
24-26 AMC Coal Convention, Netherlands Plaza Hotel, Cincinnati, Ohio.

DECEMBER 1950

7-9 Electric Furnace Steel Conference, Iron and Steel Div., Hotel William Penn, Pittsburgh.

APRIL 1951

2-4 Open Hearth and Blast Furnace, Coke Oven and Raw Materials, Conference, Iron and Steel Division, Statler Hotel, Cleveland.

mapping of the Grassy quadrangle south of Sunnyside, Utah. Headquarters are in the Federal Bldg., Salt Lake City. The report of the Mount Gunnison quadrangle, in Colorado, is being processed for publication.

Robert B. Johnston, formerly a student at the Otago School of Mines, is a mining engineer for the General Mining and Agency Co. in Kuala Lumpur, Malaya.

Jesse C. Johnson has been appointed to the newly established post of deputy manager, AEC Raw Materials Operations Office, Washington. He had been assistant manager in charge of domestic production. He will assist Manager **John K. Gustafson** in administering the entire AEC program for the acquisition and production of all raw materials including uranium, used in the national atomic energy program. **F. H. MacPherson,** former manager of the Polaris-Taku Mining Co. in Vancouver, B. C., has been appointed manager of the AEC Raw Materials Office in Grand Junction, Colo.

Helene Klein, formerly on the staff of ME, is now in Paris. When last heard from, she was vacationing in Italy, but intended to return to Paris in the fall to find a job.

Keith Kunze has taken the job of mill superintendent of the Central Eureka Foundry Co., Sutter Creek, Calif. He had been mill foreman for the Resurrection Mining Co.

Eric J. Langevad has resigned as exploration engineer for the Electrolytic Zinc Co. of Australasia to accept the post of section manager for Kenya Consolidated Goldfields, Kitere, Kenya Colony, British East Africa.

Herbert H. Lauer, plant manager of the Glens Falls Portland Cement Co. for the past 6½ years, resigned that post on Sept. 30 to go into consulting engineering with headquarters in the Land Title Bldg., Philadelphia. Mr. Lauer has had over thirty years of cement and industrial plant design, construction, operation, and management experience both at home and abroad.

S. H. Lorain, who has been chief of the Albany division mining branch of the Bureau of Mines, has transferred to the Alaska station of the Bureau at Juneau.

Frank E. Love, who has been in Alaska for the U. S. Smelting Refining and Mining Co., has returned to the States and is living in Boulder City, Nev.

R. J. Mechin, manager of the Edwards Division at Balamt, N. Y., of the St. Joseph Lead Co., has moved to the Company's New York office.

T. H. McClelland returned to Colombia on Oct. 14 after a five month vacation in the States. He resumes his post of field manager for Asnazu Gold Dredging Ltd., at Asnazu.

J. B. McKay

J. B. McKay can be reached in care of Campbell Red Lake Mines, Balmertown, Ont. He arrived there last March, getting in on the start-up of a 65-ton fluid-type roaster. Since the fluid-type roasters are not far beyond the development stage, he finds it most fascinating and when all the roasting plant problems are ironed out, there will still be plenty of work left on the metallurgy, since this may well be the most complex flow sheet of any gold mill anywhere.

Ken Merklin has been transferred to Hibbing, Minn., as Mesabi range sales representative for the Western Machinery Co. **Galen de Longchamps** recently resigned as manager of the Hibbing office to move to California.

George F. Meyer, Jr., is with the engineering division of the Empire Zinc Co., Hanover, N. Mex.

Robert A. Mitchell, with the RFC, has been transferred from Washington, D. C., to Los Angeles. His address there is 949 Mullen Ave.

Crispin Oglebay has resigned as president of Oglebay, Norton and Co. He is chairman of the board.

Khem W. Palmer, Jr., is working for the Bethlehem Collieries Corp. of Johnstown, Pa.

William C. Peters, formerly a geologist with the Empire Zinc Division of the New Jersey Zinc Co., is now on the faculty of Idaho State College as an instructor in geology. His home address is 201 Campus Drive, Pocatello.

Bruce R. Pickering is an underground mine worker for Blackwater Mines Ltd., Waiuta, New Zealand.

Victor J. Pittson, formerly on the engineering staff of the Howe Sound Exploration Co., Snow Lake division, is now with Madsen Red Lake Gold Mines Ltd., Madsen, Ont.

Morton E. Pratt, Jr., became metallurgist at the Round Mountain Gold Dredging Corp., Round Mountain, Nev., on Oct. 1. He had been research engineer for Yuba Consolidated Gold Fields.

David C. Minton, Jr.

David C. Minton, Jr., assistant to the director of Battelle Memorial Institute, has been made executive in charge of sponsor relations and projects development, acting as liaison between Battelle and industrial and governmental sponsors conducting research at the Institute. He has been with Battelle since 1941, except for a period during the war when he was in Washington with the war metallurgy committee of the National Academy of Science and National Research Council and the National Defense Research Committee of the Office of Scientific Research and Development.

Walter R. Ziebell is an instructor at the University of Miami in the department of geology, teaching mineralogy, economic geology, historical and physical geology.

Have You Done It?

Have you remembered last month's request for up-to-date information for the 1950 Directory? Have you done anything about it?

If you have a new address, a new company affiliation, a new job, please advise us. Your Directory listing will be the same as it was in the 1948 edition if you haven't brought headquarters up to date. And if and when you change that address, please include your previous address and Branch—Metals, Mining, or Petroleum—affiliation.

—In the Metals Branch—

Charles R. Cook, Jr., is working as research metallurgist for the Titanium Division of the National Lead Co. at South Amboy, N. J. His mail goes to Box 284A, RFD 1, Metuchen, N. J.

Gerrit De Vries recently moved to California where he is employed as a metallurgist with the Naval Ordnance Test Station in Pasadena. His home address is 1618 Brycedale Ave., Duarte, Calif.

R. S. French and **W. T. Toussaint,** both with the Bridgeport Brass Co., received Master of Engineering degrees from Yale last June.

John E. Fries, Jr., is with the national bearing division of the American Brake Shoe Co., Meadville, Pa.

A. F. Gallistel, Jr., has left the Minneapolis Honeywell Co., where he was a design engineer, to become chief engineer for the Perfection Mfg. Co., Minneapolis, Minn.

Paul Gordon is assistant professor of physical metallurgy in the department of metallurgical engineering at the Illinois Institute of Technology, Chicago.

James C. Hartley

James C. Hartley has been appointed a staff executive of Winchester Repeating Arms Co., a division of Olin Industries, Inc., of New Haven, Conn. He will handle special assignments for the regional manager. Mr. Hartley was vice-president and general manager of Barium Steel and Forge, Inc., and had his own metallurgical consulting office in New York City.

Earl A. Hasemeyer is employed as a metallurgical engineer by the Western Cartridge Co., East Alton, Ill.

L. E. Householder transferred from the McCook plant as chief plant metallurgist to the main office of the Reynolds Metals Co., Richmond, Va., as assistant chief metallurgist.

Robert R. Kupfer has finished work for his B.S. degree in metallurgy at Montana School of Mines and is studying for his master's degree in mineral dressing. His address is 1221 W. Porphyry St., Apt. 609, Butte.

Paul D. Merica

Paul D. Merica, executive vice-president of the International Nickel Co. of Canada, was elected a director of the Babcock & Wilcox Co. on Sept. 22.

Gilbert M. Leigh became research engineer for the Colgate-Palmolive-Peat Co., Jersey City, N. J., on Sept. 1.

C. R. Lillie, having recently completed three years of graduate work at Carnegie Tech, has taken the post of technical aide to the committee on ship steel of the National Research Council, Washington.

W. M. Mahan returned to his former headquarters at the Bureau of Mines sponge iron plant, Laramie, Wyo., after a six month transfer to the Bureau's Salt Lake City Station. The Laramie plant is in standby condition with plans for the future indefinite.

W. E. Mahin, recently appointed director of research at the Armour Research Foundation, has been made a member of the National Research Council for a three-year period. He will represent the ASM.

John D. Mitilineos graduated from the Colorado School of Mines last June and since then has been a metallurgical engineer with the American Platinum Works, Newark, N. J.

Frank C. Moran became superintendent of smelting for Mount Isa Mines Ltd., Mount Isa, Queensland, Australia, on June 1.

F. D. L. Noakes recently gave up his post as lecturer in metallurgy at the Royal School of Mines, London, to take up a new job as refinery metallurgist with the Rhodesia Copper Refineries Ltd., N'kana, Northern Rhodesia.

Edward P. Quick has been employed as a practice engineer in the blast furnace department of the Wheeling Steel Corp., Steubenville, Ohio, since graduating from Penn State last June.

W. Spencer Reid is manager of the Utah Department of the American Smelting and Refining Co., Selby, Calif., succeeding **R. D. Bradford,** who is now general manager.

Gene D. Selmanoff received his M.S. degree in metallurgy at the University of Minnesota last July. Since then he has been working for the Institute for the Study of Metals at the University of Chicago.

DuRay Smith resigned from the Union Spring and Mfg. Co., New Kensington, Pa., on June 1, to live in Phoenix, Ariz., near his small citrus grove. His search for "that place in the sun" has taken him to 3030 N. 7th St., Phoenix.

Morty Schussler

Morty Schussler is working at the gaseous diffusion plant of the Carbide and Carbon Chemical Corp., Oak Ridge, Tenn., as a metallurgist in the metallurgy division. He was with the Caterpillar Tractor Co.

Hubert C. Smith, chief metallurgist of the Great Lakes Steel Corp., has been made assistant vice-president in charge of metallurgical control. This new post was created in recognition of the increased responsibilities for production quality accompanying the plant's expansion program.

Harry H. Stout, Jr., has been made assistant director for contract administration for the Franklin Institute, Philadelphia. After service in the Army, which he left with the rank of Lieutenant Colonel in the Ordnance Department, in 1946 he became director of the new projects division of the Franklin Institute Laboratories for Research and Development.

William R. Toeplitz, who is vice-president in charge of engineering research for the Bound Brook Oil-Less

Bearing Co., has been elected to the Company's board of directors.

Alexander R. Troiano, formerly on the staff at Notre Dame, is professor of physical metallurgy at Case Institute of Technology, Cleveland, Ohio.

Roy Erwin Swift

Roy Erwin Swift, formerly of the faculty of the school of chemical and metallurgical engineering of Purdue, was awarded the degree of doctor of engineering by Yale in June. He has joined the faculty of the Mackay School of Mines at Reno to teach mining and metallurgy.

R. J. Turney can be reached at Mount Isa Mines, Ltd., Mount Isa, Queensland, Australia.

Ferdinand L. Vogel, Jr., is working for the American Smelting and Refining Co., Barber, N. J., as a research metallurgist. His permanent address is 59 Freneau Ave., Matawan, N. J.

R. U. Volterra has set up and completed the plant of the Cia. Alberto Molho Metales Preciosos in Buenos Aires and is back with the Metals and Controls Corp., Attleboro, Mass., in charge of refining operations.

Edward M. Wallace has formed a company, the Wallace Mfg. Co. in West Springfield, Mass., for the purpose of manufacturing and selling hand shears and allied products.

John P. Warner has completed his period at Kerr-Addison Gold Mines Ltd. under the Ontario Mining Association's postgraduate scheme and now has a permanent post with Falconbridge Nickel Mines Ltd. as a junior engineer in the metallurgical department.

Jonathan M. Whitmer has been working at the International Nickel Co. research laboratory, Bayonne, N. J., since his graduation from the University of Kentucky.

William F. Zerbe is vice-president in charge of operations, a newly created post of the Central Iron and Steel Co., Harrisburg, Pa., subsidiary of Barium Steel. He had been general manager of operations.

—In Petroleum Circles—

Walter K. Arbuckle has a job with the British American Oil Producing Co. as a petroleum engineer trainee. He receives mail at P. O. Box 65, Taft, Texas.

Robert M. Beatty is manager of the geological division of the American Republics Corp. at Houston, Texas.

Stanley A. Bloch is a special instructor in petroleum engineering at the University of Oklahoma, Norman.

Chester U. Burk is a mechanical engineer in the Oklahoma-Kansas division of the Continental Oil Co., Ponca City, Okla.

Robert H. Burns, formerly with the Knowlton Engineering Co., is an independent consultant on petroleum development and production in Oklahoma City, Okla.

J. R. Chestnolvick is with the Continental Oil Co., Fair Bldg., Fort Worth, Texas.

Arthur E. Creamer has the job of petroleum engineer trainee with the Gulf Oil Corp. production division. His mail goes to 1308 2nd St., Rosenberg, Texas.

L. Dean, Jr., is a junior engineer with the Pantepec Oil Co., El Roble Office, Apartado 888, Caracas, Venezuela.

Gustav Egloff, director of research for the Universal Oil Products Co., Chicago, has been elected president of the Western Society of Engineers.

H. B. Fuqua has changed his work and address from the Gulf Oil Corp., Houston, to the Texas Pacific Coal and Oil Co., Fort Worth 1, Texas.

Page O. Greene is working as an engineer for the General American Oil Co. of Texas in Odessa.

John W. Gregg is an assistant professor at the University of Alberta, Edmonton, Alta.

Brooks Hall has been transferred to Billings, Mont., to help open a new office for the Stanolind Oil and Gas Co. there.

J. M. Hansell has transferred to Calgary, Alta., as chief geologist for the Canadian division of the Sun Oil Co.

Bob T. H. Hulsey is a member of the petroleum department of the Chase National Bank, New York City.

J. B. Jones has transferred from Corpus Christi to San Antonio, Texas, to open a new office for the Halliburton Oil Well Cementing Co.

J. Pat Kidd, after graduation from the University of Oklahoma last January, began working for the Delta Drilling Co. He can be reached in care of the Company, Box 2012, Tyler, Texas.

Joseph L. Krieg recently graduated from Texas Tech and is now employed by the Transcontinental Gas Pipe Line Corp. as a progress engineer.

R. A. Legeron has been transferred by the Schlumberger Well Surveying Corp. from Houston to Calgary, Alta., where he will be Canada area manager.

J. J. Zorichak

J. J. Zorichak resumed the chairmanship of the Rangely Engineering Committee on July 15, after a year with the API Dallas office. During the war he served with the PAW, and prior to that was with Stanolind in Tulsa.

K. G. Mackenzie, assistant to vice-president of The Texas Co., was awarded a certificate of appreciation by the API at a dinner of the group's refining division in Houston.

Mahlon F. Manville is employed by the Sinclair Oil and Gas Co. He had worked for that company while attending L.S.U., from which he graduated last June.

Thomas J. McCroden received his Master of Science degree in geology at Stanford in September and took employment as a geologist in the exploration department of the Standard Oil Co. of California, San Francisco.

John A. McCutchin can now be addressed in care of the Bay Petroleum Corp., 308 8th Ave. W., Calgary, Alta.

John R. McKay is now addressed at the British American Oil Co., 209 6th Ave. W., Calgary, Alta.

Jim W. Mims, who graduated from Texas A&M in June, is now employed as a field engineer with the North Basin Pools Engineering Committee of Midland, Texas. His present residence is Denver City, Texas.

James D. Murdoch, Jr., is development and production engineer for Major Distributors Ltd., Edmonton, Alta.

Oscar C. Person is with the Magnolia Petroleum Co. at Lake Charles, La., as a petroleum engineer trainee.

George K. Peters, after graduating from the University of Pittsburgh with a B.S. in petroleum engineering in June, was employed by the Honolulu Oil Corp. in Taft, Calif., as an engineer in training.

L. Merrill Rasmussen can be reached at Box 11, Seminole, Okla. He is a student engineer with the Gulf Oil Corp.

R. J. Schneider is working with the Hughes Tool Co. in the Rocky Mountain division, stationed at Vernal, Utah. He is field man in northwest Colorado and northern Utah.

Robert R. Shaffer, who recently graduated from the University of Southern California after earning his B.S. degree in petroleum engineering, is employed by the Stanolind Oil and Gas Co. in Levelland, Texas.

Robert C. Shields is working for The Texas Co., 1115 Milburn, Odessa, Texas, as a petroleum engineer trainee.

Warren A. Sinsheimer, Jr., has the job of petroleum engineer with DeGolyer & MacNaughton, consulting petroleum engineers of Dallas.

S. Anthony Stanin received a B.S. degree in geology from the University of Utah in June and took employment with the Phillips Petroleum Co. He is at present a trainee with a seismograph unit in Wyoming, where he is addressed in care of the Company, Box 422, Lander.

Paul D. Torrey became president of Lynes, Inc., a little over a year ago and has gradually discontinued his consulting work. Lynes, Inc., is engaged in the design and development of new tools for selective chemical treatment of oil and gas wells, and for the precise control of the injection and production of fluids from wells. He devotes a good deal of his time to the application of the Company's equipment to gas-oil ratio control, for the exclusion of water, and in secondary recovery and pressure maintenance operations. A new office and plant was recently opened at 7042 Long Drive, Houston.

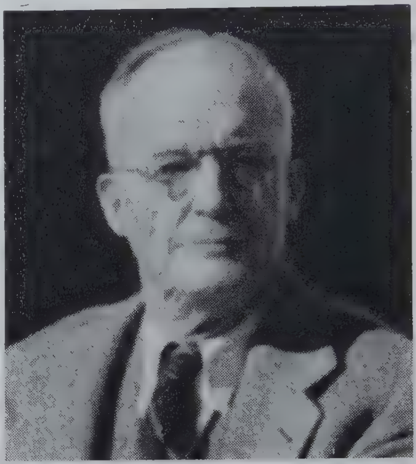
William J. Turner is working in Dallas, Texas, as a junior engineer with the Atlantic Refining Co.

Harold G. Vanhorn received a M.S. degree from Texas A&M in September. He is employed by the Shell Oil Co. as a junior exploitation engineer in the New Orleans area.

Richard H. Widmyer is a petroleum engineer trainee with The Texas Co. at New Iberia, La.

Trevor G. Williams is assistant production engineer for the Anglo-Iranian Oil Co., Abadan, S. Iran.

Obituaries



H. Norton Johnson

H. Norton Johnson (Member 1919), a geologist who had worked in New Zealand and the Philippines as well as in the States, died July 26 at his home in Santa Barbara, Calif. He was professor of geology at Westmont College at the time of his death and was considering an offer by the Afghanistan Government to head a department of geology and mining in a school that government plans to open. Dr. Johnson received degrees from Amherst, Columbia, and Harvard, the latter a doctorate in 1932. He worked for Anaconda and the U. S. Forest Service and then, in 1910, went to New Zealand to find a lost vein of gold. This venture was successful and he became general superintendent of the Consolidated Gold Fields of New Zealand. He returned to the States to work for Phelps Dodge, U. S. Smelting, General Petroleum Corp., and the Metropolitan Water District, then went to the Philippines for the National Development Co., returning in 1940.

Charles Tyndale Evans (Member 1919), chief metallurgist for the Elliott Co., died May 13, 1949. Born at Glen Moore, Pa., in 1872, he studied at Dickinson College, University of Pennsylvania, and Harvard. For twenty years he taught school and then in 1918 switched to the industrial field as chief metallurgist of the Cyclops Steel Co. in Titusville, Pa. By 1936 he was vice-president of the Universal-Cyclops Steel Corp.

Dwight Hugh Fortine (Member 1938), chief geologist for the California division of the Barnsdall Oil Co., died on Aug. 3. His death came at the age of 44 and followed the death of his wife Alice by two days. After receiving his A.B. degree from Stanford in 1926, he went to work for the Miley Exploration Co. as assistant petroleum engineer. He spent three years in Venezuela as exploration geologist for the Caribbean Petroleum Co., returning to California in 1931 to enter the employ of the Barnsdall Oil Co.

Thomas J. Barbour (Member 1897), consulting engineer of San Francisco, is dead. For many years he was president of the Barbour Chemical Works. In the 1920's he opened a consulting office in San Francisco.

Russell Johnson Parker

AN APPRECIATION BY ANTON GRAY

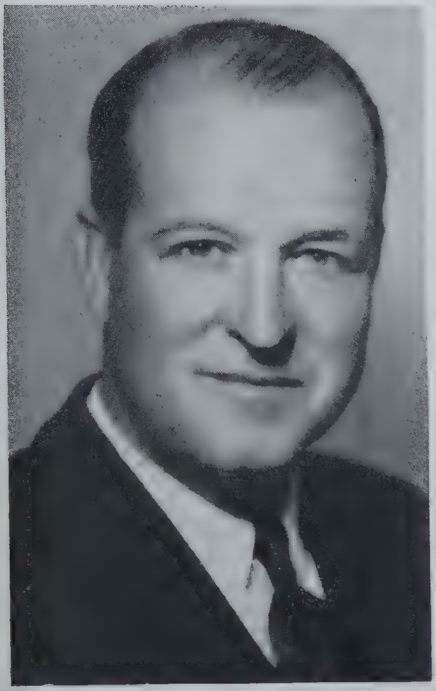
Russell Parker (Member 1944) died Sept. 9 in the crash of a Quebec Airlines plane that took the lives of two other Kennecott officers. Russell Johnson Parker was born in Olney Springs, Colo., and received his education in mining engineering at the Colorado School of Mines, graduating in 1919. Shortly after leaving the School of Mines, he went to the Belgian Congo. There he was engaged in diamond prospecting and production for the Foretminiere.

About 1925, Mr. Parker became interested in the copper possibilities of Northern Rhodesia, about which very little was known at that time. He went to London, joined A. Chester Beatty in the Selection Trust, Ltd., and was associated with that group until he came to the United States in 1940. While with the Selection Trust he examined for them the copper prospects of Rhodesia, and it is almost wholly due to his recognition of the possibilities of these deposits that led the Selection Trust to undertake the developments which resulted in the successful operations now known as the Roan-Antelope and Mufulira mines.

Shortly before the war, Mr. Parker

Necrology

Date Elected	Name	Date of Death
1937	Army Adams	Aug. 20, 1949
1940	Ralph M. Bowman	June 18, 1949
1946	George F. Campbell	June 18, 1949
1944	H. M. Faust	Sept. 19, 1949
1903	Herbert C. Greer	August, 1948
1919	H. Norton Johnson	July 26, 1949
1917	James D. Jones	Unknown
1930	J. H. G. Monypenny	1949
1921	Sydney L. Palmer	May 9, 1949
1916	Rudolph Porter	July 10, 1949
1926	Arthur M. Robinson	June 27, 1948
1938	Joseph M. Thiel	July 16, 1949
1937	Joseph A. Tennant	Unknown
1918	John E. Thomas	Aug. 20, 1949
1914	Arno S. Winther	Unknown
1918	Fred L. Wolf	Sept. 27, 1949
1936	Joseph C. Yob	Feb. 18, 1949



Russell J. Parker

Earl T. Stannard

Arthur D. Storke

was made managing director of the Consolidated African Selection Trust, and he left his position in 1940 to come to the Kennecott Copper Corp. as assistant to the president. In 1948 he was made a vice-president of Kennecott, and put in charge of the Canadian titanium development.

Russell Parker's achievements in his profession, as indicated in this very brief outline, were many, but his greatest achievements were not technical. In Africa, in London, in Colorado, and in New York all the people with whom he worked became and remained his friends. The greatest tribute that has been or can be paid him is the inquiry that has been made wherever he has worked, "When is Parker coming back?"

Earl Tappan Stannard

An Appreciation by C. T. Ulrich

Earl Stannard (Member 1920) was killed Sept. 9 in the crash of a Quebec Airways plane. Earl Tappan Stannard was born in 1882 at Chittenango, N. Y. He attended the Sheffield Scientific School at Yale and graduated in 1905 in the mining course. He then continued for one additional year in the graduate school.

His first experience after leaving Yale was with the Federal Lead Co. in Missouri. In 1911 he was employed by the Braden Copper Co. in Chile and for three years was general superintendent of concentrators and, as such, was in charge of both construction and operation of the mills.

In 1914 he left Chile for Alaska, subsequently becoming manager of both the Kennecott and Latouche properties of the Kennecott Copper Corp., with general supervision over the railroad which served the mines at Kennecott.

In 1920 he went to Seattle as general manager of the Kennecott properties located in Alaska, of the Alaska Steamship Co., and of the Copper River and Northwestern Railway Co. In 1923 Mr. Stannard was made vice-president of the Kennecott Copper Corp. and in 1929 he moved to New York where he also became vice-president of Braden Copper Co. and of other subsidiaries. In May, 1933, Mr. Stannard was elected president of Kennecott and Braden and continued in these positions until the day of his death. He was also, for a number of years, a director of J. P. Morgan & Co. and the Johns-Manville Corp.

In 1936 an honorary degree of Doctor of Engineering was conferred upon him by the Michigan College of Mining and Technology. In 1937 the King of Belgium named him a Commander of the Order de la Couronne.

Endowed with a keen mind and sound business judgment, he was also possessed of the highest principles and a gracious and charming personality. A man of great energy and capacity for work, he gave unsparingly of his time and efforts. All these admirable qualities combined to make him a wise and effective leader of the Corporation and an outstanding personality in the industry, not only in the United States and Chile, but throughout the world.

Arthur D. Storke

An Appreciation by Fred Searls, Jr.

Arthur D. Storke died Sept. 9 in the Quebec Airways tragedy that took the lives of 22 other persons, including two of his colleagues, officers of the Kennecott Copper Corp.

Arthur Storke was born at Auburn, N. Y., May 21, 1894. He attended Leland Stanford in 1913, and the University of Colorado in 1914 and 1915.

In 1916, he entered the employ of Climax Molybdenum and in 1917 became assistant superintendent. The rigors of the Climax location impaired his health and the American Metal Co., which even at this early date appreciated his character and ability, was glad to transfer him to Joplin as its local representative.

In 1918, he enlisted in the 27th Engineers, an exceptional regiment of army troops formed, like the British tunneling companies, for mine warfare and combat shelter construction.

On demobilization, Storke worked out of San Francisco as an independent engineer and, with Carl O. Lindberg and others, on the examination and management of properties from Central America to Alaska until the end of 1925. In 1926, Climax having re-opened in 1925, he returned to that operation as general superintendent. There he not only made prompt improvement in the mining methods, but initiated development work that in 1927 led to the discovery of the present large orebody. In that year, he was again transferred to the American Metal Co., and proceeded to Africa, as assistant to H. S. Munroe.

His confirmation of the favorable opinion of the Rhodesian copper belt in sedimentary rocks, held in early 1928 by few American engineers, other than Parker, Sussman, and one or two more, insured participation by the American Metal Co. in the financing of Roan Antelope and the projects that later were included in Rhodesian Selection Trust.

Storke's part in bringing into production the Roan and Mufulira properties during 1929 and the dark days that followed it, are well known to the mining fraternity on both sides of the Atlantic; but perhaps only the relatively few remaining American engineers, who were involved in these and the contemporaneous efforts at Rhokana, can fully realize the problems—not only of mining methods and metallurgy, but also of native labor, personnel from three nations, colonial government relations, and distance from base, with which the early stages of these developments had to struggle. As D. D. Irwin writes, his success was "a tribute to personality, tact, all-around ability, and good judgment." His energy and capacity are evidenced by the fact that before these operations were in full swing, Storke also functioned as managing director of Selection Trust, controlling the management of the totally different operations of Trepca and Beatty's alluvial diamond mines.

Storke's services to England, his adopted country, during the recent war will probably never be fully known for much of it was in Air Force intelligence; but it is fair to say that his work as mineral adviser to the Ministry of Supply was outstanding and, of itself, well merited his decoration as C.M.G. by the King in 1947 "for mining development in the Colonial Empire."

It is perhaps less generally known that Storke's early recognition of the possibilities of the O'okiep District and, particularly, his more recent vigorous espousal of the purchase and unwatering of the Tsumeb property in South West Africa, had much to do with the success of these enterprises.

However, this is an appreciation, not a biography. Kennecott has lost the services of a man who would have upheld its leadership and its traditions, and carried them further; and as future services are worth most in the future, Kennecott has lost the most. But it is perhaps we in the Metal Company and Newmont, who have known Storke longer, who have been in the past, and recently, beneficiaries of his initiative, ability, and judgment, who have sat with him as directors and friends, and worked with him on common problems—it is perhaps we who will most miss his cheery smile and his quiet words of wisdom and good sense. God give him the rest he has earned.

Arthur Michael Robinson (Member 1926), mining consultant whose work had taken him all over the globe, died in England on June 27, 1948. He was born at Clitheroe, England, in 1892. The first World War interrupted his studies at the Royal School of Mines but he received his degree in 1920. His first mining job was in Ireland; then he returned to London to work for the Palmer Foundry and Engineering Co. and later for the "SG" Minerals Syndicate Ltd. In 1924 he went to Par Treves, France, as chief surveyor to the Mines de Villemagne. In the 1930's he worked for Mount Isa Mines, New Guinea Goldfields and Gold Coast Banket Areas Ltd. and since then had done consulting work.

Alfred Clark Stoddard (Member 1917), chief mining engineer for the Inspiration Consolidated Copper Co., died on July 15. He joined the Inspiration staff in 1912 and worked for the Company until his death. Born at Denver in 1879, he received his M.E. degree from the Michigan College of Mines. He had worked for the O.D. Copper Mining and Smelting Co. and the New York and Honduras Rosario Mining Co.

Joseph A. Tennant (Member 1937), president of the Tennant Co. of Houston, is dead. After receiving his B.A. degree from the University of Texas and his S.B. degree from MIT, he became industrial engineer for the Rochester Railway and Light Co. After a year as consulting city engineer for Houston, he became president of the consulting engineering concern that bore his name. He was also vice-president of the Abercrombie Pump Co. and the Rio Grande Eastern Railway Co.

Joseph Mathias Thiel (Member 1938), mining geologist, died at Joplin, Mo., on July 16, 1949, following several months' illness. He was born in St. Paul, Minn., on March 3, 1899, and was a graduate of the University of Minnesota School of Geology. Practically all of his professional career was spent in the Central States, first with the Wisconsin Geological Survey, then for nearly ten years, beginning in 1920, with the Missouri Geological Survey where he was in charge of its Joplin branch. He then worked with the U. S. Geological Survey for nearly two years. In 1935, Mr. Thiel joined the geological staff of George M. Fowler, Consulting Geologist, where he was employed continuously until his death. The excellence of Mr. Thiel's work is attested in many maps and other data that were published by the Missouri Geological Survey and in thousands of his recorded observations pertaining to the stratigraphy of the Tri-State mining district.

John Elmer Thomas (Member 1918), widely known oil man and geologist, died Aug. 20 in Fort Worth, Texas. He had returned only recently from Italy where he investigated the oil reserve of the Po Valley for the Italian Government. Mr. Thomas, a native of Ohio, began his career, after graduating from the University of Chicago, with AS&R. He served as geologist for several oil companies and in 1917 went into consulting work. He was a member of the volunteer committee on petroleum economics for the Federal Oil Conservation Board and later was associate chief of the fuel section of the OPA. He also served as special assistant to the deputy petroleum co-ordinator.

Charles Erb Wuensch

An Appreciation by
Philip J. McGuire

Charles Erb Wuensch, familiarly known as "Erb" to his many and widely distributed friends throughout the Western mining world, died Aug. 27 in San Francisco. In his 57 years he firmly established his ability as an inventor and an engineer. He was always eager to help anyone in need and his friendliness and generosity will be greatly missed by all who knew him.

Mr. Wuensch received an E.M. degree from Colorado School of Mines in 1914 where he participated in athletics and showed early technical talent. After two years' experience with Empire Zinc, he went to Central America for a year on geological work. Subsequent engagements were with Thane Exploration Co., American Smelting & Refining, U. S. Smelting, and consulting work up to 1927.

Locating then in Joplin, Mr. Wuensch became so interested in making the Missouri-Kansas Zinc Corp. a success that he developed the differential density (heavy media) sink float process that has since come into wide general use.

The move from Joplin, Mo., to San Francisco was made about 1940. Since then, consulting work in mining and metallurgy in the United States, Mexico, and Central America took up part of his time. However, the primary interest throughout the life of Mr. Wuensch was invention, which he pursued with tremendous energy along many lines. Besides the sink float process mentioned above which is at present his best known development, his inventive mind covered a wide range of ideas. He also contributed technical articles for publication to advance the development and general knowledge on many of the above subjects.

The mining industry will miss his untiring energy and inventive enthusiasm and his friends will miss even more the man himself, sociable, kindly and generous.

Proposed for Membership

Total AIME membership on Sept. 30, 1949, was 15,988; in addition 4427 Student Associates were enrolled.

ADMISSIONS COMMITTEE

James L. Head, Chairman; Albert J. Phillips, Vice-Chairman; George B. Corless, T. B. Counselman, Ivan A. Given, Robert L. Hallett, Richard D. Mollison, and John Sherman.

Institute members are urged to review this list as soon as the issue is received and immediately to wire the Secretary's Office, night message collect, if objection is offered to the admission of any applicant. Details of the objection should follow by air mail. The Institute desires to extend its privileges to every person to whom it can be of service but does not desire to admit persons unless they are qualified.

In the following list C/S means change of status; R, reinstatement; M, Member; J, Junior Member; AM, Associate Member; S, Student Associate; F, Junior Foreign Affiliate.

ARIZONA

Ajo — PAPKE, KEITH GEORGE. (C/S—S-J). Assistant engineer, Phelps Dodge Corp.

Hayden—OWEN, JOHN WILLIAM. (C/S—S-J). Junior engineer, Kennecott Copper Corp.

Morenci — ALEXANDER, ALBERT LEONARD. (C/S—S-J). Assistant shift foreman, Phelps Dodge Corp.

Superior—PETERSON, ROY ERNEST. (C/S—S-J). Trainee, Magma Copper Co.

ARKANSAS

Malvern—ALLEN, ROBERT ALVA, JR. (J). Mineralogist, Baroid Sales Division, National Lead Co.

State College — KEETON, JOHN RICHARD. (C/S—S-J). Engineering instructor, Arkansas State College.

CALIFORNIA

Alhambra — ALLINDER, WILLIAM FREDERICK. (C/S—S-J). Petroleum engineer, Seaboard Oil Co. of Delaware.

Altadena — SLATTERY, HARRY WILLIAM. (J). Engineer, Oil Properties Consultants.

Bakersfield—ARMBRUSTER, EARL AUGUST. (M). Division exploitation engineer, Shell Oil Co. BETHEL, FRANKLIN THOMAS. (C/S—S-J). Senior core analyst, Superior Oil Co.

Bellflower — FULLERTON, HAL BRADFORD, JR. (C/S—S-J). Engineer in training, The Texas Co.

Concord—VOGT, WILLIAM A. (M). Project engineer, Kaiser Engineering, Inc.

Hollywood—RIEGLE, JOHN, JR. (M). Petroleum engineer, Southern California Gas Co.

Long Beach—KEALER, RAYMOND CHESTER. (M). Self employed. VOGEL, LEE CHARLES. (J). Chemist. Oil Well Research, Inc.

Montrose—WHITLOCK, REGINALD RAY. (C/S—S-J).

Playa Del Rey—GRANER, JESSE BLAINE. (C/S—S-J). Petroleum engineer, Graner Oil Co.

San Francisco — WEBER, MARY HILL. (J). Mining geologic aid, California Division of Mines.

San Leandro — LAMBERT, EARL FREEMAN. (C/S—S-J). Assistant geologist, San Luis Mining Co.

South Gate — EDSON, THOMAS FARRER. (M). Executive vice-president, A. R. Mass Chemical Co.

Walnut Creek—BRUTON, WILLIAM CHARLTON. (AM). District sales manager, American Manganese Steel Division, American Brake Shoe Co.

Whittier—ATKINS, EARLE RICHARDSON, JR. (J.) Associate production engineer, Union Oil Co. of California. MONROE, REX. (C/S—J-M). District sales manager, refinery division, Sivyer Steel Casting Co. PRESTON, FLOYD W. (C/S—S-J). Assistant research engineer, California Research Corp.

COLORADO

Climax—LEINON, CLYDE HENRY. (C/S—S-J). Engineer, Climax Molybdenum Co.

Denver—RITTER, ETIENNE ALPHONSE. (R—M). Mining engineer, Cripple Creek Mines.

Durango—ROBERTS, DAVID. (C/S—J-M). Major, Corps of Engineers, U. S. Army.

Golden — SINHA, BINDESHWARI NARAIN. (AM). Assistant geologist, Geological Survey of India.

Ouray—HALLOCK, JOHN ROBERT. (C/S—S-J). Mill helper, Idarado Mining Co. TAYLOR, I. ROBERT. (C/S—S-J). Sampler, Idarado Mining Co.

CONNECTICUT

Bridgeport—STEVENS, MARSHALL WILLIAM. (C/S—S-AM). Foundry metallurgical engineer, General Electric Co.

Greenwich—STARR, H. DANFORTH. (AM). Assistant to president, Cerro de Pasco Copper Corp.

Plymouth—TROUT, DELMAR EVERETT. (C/S—S-J). Metallurgist, Scovill Mfg. Co.

Stamford—WARK, CARLOS RICHARD. (C/S—J-M). Metallurgical engineer, American Cyanimid Co.

DISTRICT OF COLUMBIA

Washington — ONODA, KIYOKO. (C/S—S-J). Mineralogist, U. S. Geological Survey.

FLORIDA

Plant City — CATHCART, JAMES BACHELDER. (C/S—J-M). Geologist, project chief, Florida phosphate, U. S. Geological Survey.

GEORGIA

Gainesville — CASTLEBERRY, DOUGLAS. (C/S—S-J).

IDAHO

Kellogg—LOMAS, RAYMOND EDWARD. (M). Mine superintendent, Sunset Minerals, Inc.

ILLINOIS

Alton—HASEMEYER, EARL ALBERT. (C/S — S-J). Metallurgist, Western Cartridge Co.

Chicago—ELLIS, JOSEPH MATTHEW. (C/S—S-J). Equipment test engineer, Ingersoll-Rand Co. FREY, E. LEE, JR. (C/S—S-J). Plant metallurgist, micro-cast division, Austenal Laboratories. GLASSER, JULIAN. (M). Research metallurgist, Armour Research Foundation. HEIKKINEN, LILIAN MAY. (C/S—S-J). Laboratory technician, Institute for the Study of Metals, University of Chicago.

Chicago Heights—SHUBERT, FRANCIS LAWRENCE. (C/S — S-J). Metallurgist, Combustion Engineering-Superheater, Inc.

Elmhurst—FOOTE, FRANK G. (C/S—J-M). Division director, Argonne National Laboratory.

Galena—DALE, CLAUDE OLIVER. (C/S—J-M). Mining engineer, Eagle Picher Mining and Smelting Co.

INDIANA

Bloomington — BARUA, VICTOR FELIX. (J). Assistant geologist, Ground Hog unit, American Smelting and Refining Co.

Crown Point — GORSKI, RICHARD ALFRED. (C/S—S-J). Foreman relief trainee, Carnegie-Illinois Steel Corp.

East Chicago—BARRETT, DONALD J. (J). Mill trainee, Inland Steel Co.

Gary — MICKELSON, CEDRIC GROPPER. (C/S—J-M). Research metallurgist, American Steel Foundries.

Hammond—MORTON, RAYMOND LEWIS. (C/S—S-J). Staff assistant, blast furnace, Wisconsin Steel Works, International Harvester Co.

Indianapolis — SHERWOOD, SAMUEL FERGUSON. (AM). Assistant to the president, Central Indiana Coal Co.

Linton — DUKES, WILLIAM WEAVER. (M). Design engineer, Central Indiana Coal Co. and Sherwood-Templeton Coal Co.

Whiting—BAUMANN, GEORGE M. (C/S—J-M). Assistant to the manager, Federated Metals division, American Smelting and Refining Co.

IOWA

Fort Dodge—HARVEY, ALFRED S. (C/S—S-J). Chief of party, Glenn H. Miller.

KANSAS

Eureka—HAUGH, WENDELL JOE. (M). District engineer, Tidewater Associated Oil Co.

Great Bend—TERRY, LOUIS LYMAN. (R, C/S—S-M). Electric pilot engineer, Dowell Incorporated.

Holyrood — HARRY, EDWARD BROOKE, JR. (C/S—S-J). Engineer trainee, Sohio Petroleum Co.

Hutchinson—COSHOW, ROBERT G. (C/S — S-J). Production engineer, Skelly Oil Co.

Sunflower — CASSIDA, WALTER. (C/S—S-J). Core drill supervisor, Continental Oil Co.

Wichita — DICKEY, LEONARD CLAUDE. (C/S — S-M). Petroleum engineer, U. S. Air Force. SPRINGER, FREDERICK MICHAEL. (C/S—S-J).

KENTUCKY

Henderson—CHARLEY, THEODORE EUGENE. (C/S—J-M).

LOUISIANA

Grand Isle — TRUBY, LESTER GEORGE, JR. (C/S—S-J). Junior petroleum engineer, Humble Oil and Refining Co.

Jefferson Parrish — HANSEN, CHRISTIAN ANDREAS, JR. (J). Junior petroleum engineer, Humble Oil and Refining Co.

Lafayette—AULICK, BURTON WILSON. (M). Division engineer, Halliburton Oil Well Cementing Co.

Monroe—BROWN, KERMIT EARL. (C/S—S-J). Junior petroleum engineer, Stanolind Oil and Gas Co.

Shreveport — CRAIG, WILLIAM LAIRD. (C/S—J-M). Production engineer, Arkansas Louisiana Gas Co. FOWLER, HENRY FLOREY. (C/S—J-M). Chief zone geologist, Gulf Refining Co.

MARYLAND

Sparrows Point—STOTT, CHARLES T. (C/S—J-M). Test engineer, Bethlehem Steel Co.

University Park — PANEK, LOUIS ANTHONY. (C/S—J-M). Roof control research engineer, Bureau of Mines.

MASSACHUSETTS

Belmont—OBERG, FRED NELSON. (C/S—J-M). Research engineer, Division of Industrial Co-operation, MIT.

Westboro—JOHNSON, CARL GUNNARD. (M). Associate professor, Worcester Polytechnic Institute; vice-president, Presmet Corp.

MICHIGAN

Dearborn—THOMAS, JOHN MARION. (C/S—S-J). Metallurgical engineer, Hoskins Mfg. Co.

Detroit—PRAKKEN, JOHN COOK. (C/S — S-J). Plant metallurgist, Chrysler Corp.

Pontiac — HEID, WILLIAM KENNEDY. (C/S—S-J). Foreman, Pontiac division, General Motors Corp.

Ypsilanti — RAYNOR, CLARENCE LeROY. (C/S—J-M). Metallurgical supervisor, Hoskins Mfg. Co.

MINNESOTA

Duluth—MIELKE, MORRIS VERNE. (C/S—J-M). Assistant concentration engineer, Oliver Iron Mining Co.

Hibbing—SUDASNA, PISOOT. (C/S—S-J). Mining engineer, Hibbing-Chisholm district, Oliver Iron Mining Co.

Minneapolis—DeMONEY, FRED W. (J). Instructor, University of Minnesota.

Nashwauk — VIANT, MELVIN LeROY. (C/S—S-M). Mine engineer, Cleveland Cliffs Iron Co.

St. Paul — BECK, WARREN RANDALL. (M). Section leader, Minnesota Mining and Mfg. Co.

Virginia — WEILER, CHARLES T. (C/S—J-M). Industrial engineer, Inter-State Iron Co.

Winona—BROM, LEO JOHN (C/S—J-M). Metallurgist, Brom Machine and Foundry Co.

MISSOURI

Annapolis—SUTTON, GLEN WOOD. (J). Industrial engineer, Tennessee Coal, Iron and Railroad Co.

Bonne Terre — PETERSEN, KENNETH CHARLES. (J). Surveyor, St. Joseph Lead Co.

Desloge — HARTER, WARREN FRANCIS. (C/S—S-J). Surveyor, St. Joseph Lead Co.

Flat River — SORKIN, JEROME HERBERT. (C/S—S-J). Surveyor, St. Joseph Lead Co.

Fulton—ANDERSON, GEORGE McCRAE. (C/S—S-J). Mining engineer, Harbison-Walker Refractories Co.

Kirkwood — FASER, JACK FRED. (R, C/S—S-J). Sales engineer, Ingersoll-Rand Co.

Overland — MOULTON, BERNARR GAMMILL. (R, C/S-J-M). Sales engineer, Ingersoll-Rand Co.

Potosi—CHANEY, JAMES BYRON. (C/S—S-J). Engineer, Baroid Sales Division, National Lead Co.

Rivermines — McHENRY, L. CHARLES. (C/S — S-J). Engineer, Tennessee Coal, Iron and Railroad Co. WAGNER, RICHARD EDWIN. (R—M). Geologist, St. Joseph Lead Co.

Rolla—HASKELL, DONALD FORREST. (C/S—S-J).

St. Louis—GEHLSEN, REIMER G. (M). Sales manager, Joy Mfg. Co.

Sedalia—QUINN, JOSEPH S. (C/S—S-J). Engineer in training, Allis-Chalmers Mfg. Co.

Webster Groves — GOSEN, JOHN WILLIAM. (C/S—S-J).

MONTANA

Butte—SIMPKINS, GEORGE ROBERT. (C/S—S-J). Assistant mining engineer, Anaconda Copper Mining Co.

Cut Bank—LADD, J. BERTRAM. (C/S — S-J). Petroleum engineer trainee, The Texas Co.

Great Falls — ALF, ALFRED IMMANUEL. (R, C/S—JA-M). Superintendent, zinc electrolyzing and cadmium departments, Anaconda Copper Mining Co. GRAHAM, THOMAS KENNEDY. (M). Assistant superintendent of zinc plant, Anaconda Copper Mining Co. JACKSON, MERYL ARTHUR. (M). Chief chemist, Anaconda Copper Mining Co. SMITH, JAMES FRANCIS. (R, C/S—JA-M). Assistant superintendent, copper refineries, Anaconda Copper Mining Co. WEVER, GUY THOMAS. (M). Superintendent of indium and rare materials department, Anaconda Copper Mining Co.

NEVADA

Reno—WELLS, ROBERT LEWELLYN. (J).

Searchlight—MOORE, FRANK CHARLES. (C/S — S-J). Engineer, Searchlight Homestake Mining Co.

NEW JERSEY

Franklin — ANTONIDES, LLOYD EARL. (C/S—S-J). Level boss, New Jersey Zinc Co.

Newark — ROSTOSKY, ANDREW, JR. (C/S—J-M). District manager, Mechanization, Inc.

Rahway—MILLER, MARTIN STANLEY. (C/S—S-J). Research metallurgist, Crucible Steel Co. of America.

NEW MEXICO

Albuquerque—BRADISH, BEVERLY B. (C/S—J-M). District geologist, Skelly Oil Co.

Carlsbad—GALE, CARLOS. (C/S—AM-M). Granular plant foreman, U. S. Potash Co.

Eunice—JAMES ROBERT KING. (C/S — S-J). Petroleum engineer trainee, Magnolia Petroleum Co.

Silver City—WHITE, ATHINGTON. (R, C/S—JA-M). Chief engineer, American Smelting and Refining Co.

Vanadium — FLEISHER, GEORGE GORDON. (R, C/S—S-AM). Engineer, American Smelting and Refining Co. GERWELS, RICHARD PAUL. (C/S—J-M). Head mine engineer, U. S. Smelting Refining and Mining Co. HARDIE, BYRON SIDNEY. (C/S—J-M). Geologist, Ground Hog Unit, American Smelting and Refining Co. PURVIS, DONALD RUSSELL. (C/S—J-M). Mine superintendent, American Smelting and Refining Co.

NEW YORK

Balmat—CAREY, DON WILLIAM. (C/S—S-J). Mine captain, St. Joseph Lead Co.

Brooklyn — FRANK, LEONARD. (C/S—S-J).

Congers — SULLIVAN, EDWARD GUY. (C/S—J-M). Assistant superintendent, New York Trap Rock Corp.

Garden City — BRAZEAU, WILLOUGHBY FRANCIS. (M). President, International Selling Corp. and Intsel Metals Corp.

Larchmont — COULTER, HAROLD BOYD. (M). Chief mechanical engineer, The Dorr Co.

Manhasset — LEE, PERCY GOODELL. (AM). General purchasing agent, Phelps Dodge Corp.

New York — KELLOGG, HERBERT HUMPHREY. (C/S—J-M). Assistant professor of mineral engineering, Columbia University. KENDALL, ERNEST GEORGE. (C/S—S-J). Instructor, Polytechnic Institute of Brooklyn. McAULIFFE, HENRY EUGENE, JR. (C/S—S-J). Petroleum engineer, Socony-Vacuum Oil Co.

Scarsdale — KENT, JAMES, KENNETH. (M). Patent counsel, American Smelting and Refining Co.

OHIO

Barnesville — EDGAR, ROBERT LOWELL. (M). Manager of sales, Watt Car and Wheel Co.

Cleveland — HAMILTON, GAIL BYRON, JR. (C/S—S-J). Steel foundry engineer, General Electric Co.

Cleveland Heights—VACTOR, HOWARD. (C/S—S-J). Petroleum geologist, R. L. Martin Oil Co.

Columbus—VANCE, CALBERT LEE. (M). Research engineer, Battelle Memorial Institute.

Lorain — JOHNSTON, THOMAS GEORGE, JR. (C/S—S-J). Junior metallurgist, National Tube Co. KETTERER, EDWARD FERDINAND. (C/S—J-M). Assistant chief metallurgist, National Tube Co.

New Philadelphia — EDWARDS, PAUL KENNETH. (C/S—S-J). Engineer in training, Allis-Chalmers Mfg. Co.

St. Clairsville — GIBSON, OSCAR CLYDE. (M). Mine superintendent, Hanna Coal Co. PRUDENT, NORMAN CHARLES. (M). General superintendent, deep mines, Hanna Coal Co.

Wellington — ANNEY, FRANKLIN WILLIAM. (C/S—S-J). Junior metallurgist, National Tube Co.

Worthington — FRAZIER, ROBERT HARRISON. (C/S—J-M). Research engineer, Battelle Memorial Institute.

Youngstown — DeHETRE, JOHN PHILIP. (C/S—J-M). Manager, oil country tubular sales, Youngstown Sheet and Tube Co. HOLSTEIN, EDGAR RALPH. (C/S—J-M). General foreman, Carnegie-Illinois Steel Corp.

OKLAHOMA

Bartlesville — FENTRESS, GEORGE H. (C/S—S-J). Technical trainee in geology (seismic), Phillips Petroleum Co.

Drumright — PHELPS, WARREN DONALD. (C/S — S-J). Petroleum engineer, Magnolia Petroleum Co.

Henryetta—MORGAN, JACK ALLEN. (C/S—S-J). Junior petroleum engineer, Sun Oil Co.

Nowata — BUCKWALTER, FREDERICK CLARK. (C/S—J-AM). Production foreman, Shell Oil Co.

Tulsa — BLYNN, RALPH G. (M). Petroleum engineer, Stanolind Oil & Gas Co. SCHOENECK, WILLIAM EDWARD. (C/S—J-AM). Vice-president of production and engineering, British-American Oil Producing Co.

OREGON

Medford — INGLE, HUGH COCHRANE, JR. (C/S—S-J). Surveyor, Hugh C. Ingle, Engineering Office.

Roseburg—OSBORNE, JAMES GILLIAM, JR. (C/S—S-J). Geologist, Shell Oil Co.

PENNSYLVANIA

Beaver — BEEKEN, ALFRED D. (M). Metallurgist and sales manager, Vulcan Crucible Steel Co.

Bethlehem—GAULT, HUGH RICHARD. (C/S—J-M). Associate professor of geology, Lehigh University.

Bradford — PAYNTER, WARREN THOMAS. (C/S—S-J). Assistant petroleum engineer, South Penn Oil Co.

California — CONRAD, OLEN EUGENE. (C/S—S-J). Time study observer, Vesta Shannopin coal division, Jones and Laughlin Steel Corp.

Indiana—GRAY, ALLEN DANIEL, JR. (C/S—S-J). Trainee, Rochester and Pittsburgh Coal Co. McCHESNEY, DAVID W. (R, C/S—S-AM). Cleaning plant foreman, Rochester and Pittsburgh Coal Co.

Kingston—SEMKO, PAUL. (C/S—S-J). Chief of party, Pennsylvania Turnpike Commission.

Lebanon — DONALD, DOUGLAS DUNN. (C/S—J-M). Chief engineer, Annville Stone Co.

New Kensington—CLINE, CHARLES WILLIAM. (C/S — J-M). Research metallurgist, Aluminum Co. of America. STUMPF, HARRY C. (C/S—J-M). Research metallurgist, Aluminum Co. of America.

Oil City — CURRENT, FARMER LEE. (R, C/S—S-M). Assistant chief metallurgist, Oil Well Supply Co.

Philadelphia — HUBBARD, ERLE JAMES. (C/S—J-M). Foundry manager, Janney Cylinder Co.

Pittsburgh — FISHER, RICHARD KEISER. (C/S—S-J). Technical representative, explosives division, American Cyanamid Co. HOGG, GORDON AUBREY. (M). Petroleum engineer, Kuwait Oil Co. STEWART, JOHN MORGAN. (AM). Vice-president, Hickman Williams & Co.

Tarentum—KOH, P. K. (C/S—J-M). Research engineer, Allegheny-Ludlum Steel Corp. SHUMAKER, MURRAY BYRON. (C/S—S-J). Research metallurgist, Aluminum Co. of America.

Tower City — BURKERT, DONALD HENRY. (M). Mine superintendent, Markson Coal Co.

Verona — STEWART, J. WARREN. (C/S—J-AM). Product metallurgist, Homestead works, Carnegie-Illinois Steel Corp.

Wilkes-Barre — ASH, RICHARD LAWRENCE. (C/S—J-M). Sales representative, Atlas Powder Co.

SOUTH DAKOTA

Belle Fourche — ELSLEY, BYRON COOPER. (C/S—J-M). Assistant superintendent, bentonite properties, Baroid Sales Division, National Lead Co.

TEXAS

Amarillo—WISHNICK, JOHN HARRISON. (C/S—S-J). Vice-president, oil and gas division, Witco Carbon Co.

Bellaire—CRAMER, ALAN CAMPBELL. (M). Assistant manager, Gulf Coast Division, Baroid Sales Division, National Lead Co.

Borger—GARWOOD, GEORGE LYMAN. (C/S—J-M). Engineer, Phillips Petroleum Co.

Corpus Christi—BROWN, CHARLES J., II. (C/S—S-J). Petroleum engineer, Heep Oil Corp.

Dallas — CRAM, EDWARD CHARLES. (M). Regional geologist, Magnolia Petroleum Co. HOLOGA, DANIEL CASIMIR. (J). Junior engineer, Atlantic Refining Co. SALE, RICHARD BARKSDALE. (M). Drilling superintendent, Seaboard Oil Co. of Delaware. SANDERS, CHARLES HORACE. (M). Assistant southwestern district manager, Cooper Bessemer Corp. SCHULTZ, FRANK AUGUST. (C/S—J-M). Vice-president, Delhi Oil Corp.

El Campo—GAINES, TOM. (C/S—J-M). District petroleum engineer, The Texas Co.

El Paso—GODSEY, EDWIN SPENCER. (C/S—S-J). Draftsman, American Smelting and Refining Co. LEE, WILLIAM Y. (C/S—S-J). Engineering draftsman, U. S. Ordnance. MILLER, MALLORY LEVI. (AM). District sales manager, Colorado Fuel and Iron Corp. MITCHELL, STERLING ROSS. (M). Consulting engineer, Lance and Mitchell. RINTELEN, JOSEPH CHARLES, JR. (M). Associate professor of metallurgy, Texas Western College.

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Titanium Investigations: Research and Development Work on the Preparation of Titanium Chloride and Oxide from Titanium Mattes*

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Introduction

This report describes the progress made in the research work on the development of a new method for preparing lower-cost titanium tetrachloride and preparing titanium oxide pigment.

One of the requirements for the commercial production of ductile titanium in the process used by the Bureau of Mines is a source of lower-cost titanium tetrachloride.

The production of ductile titanium by a modification of the Kroll[1] process, recently developed by the Bureau of Mines, requires such a source of lower-cost titanium tetrachloride to make it commercially feasible. This report describes the progress of work done at the Mississippi Valley Experiment Station at Rolla, Missouri, on the development of a new method for preparing titanium tetrachloride. During the course of this research a new method for preparing pigment-grade titanium oxide was developed.

At present, the price of technical-grade titanium tetrachloride is $0.32 a pound, which makes the price of the contained titanium $1.28 a pound.[2] In addition, the titanium tetrachloride must be purified further before it is suitable for processing into metal, thus making its cost still higher.[3]

There were 8,562 tons of rutile produced in the United States in 1947, which was 900 tons in excess of that consumed. In addition there were 13,937 tons in various stocks, exclusive of the stocks in the Government strategic stock pile.

No estimates of the domestic production of rutile are given for any of the prewar years. However, in 1939, 442 tons of rutile were imported as compared to 14,307 tons in 1947.

One of the reasons for the large increase in the production of rutile is the working of the Florida beach sands for ilmenite, during which a considerable amount of rutile is produced as a by-product.

It would be of value to determine methods for utilizing the excess production of rutile.

The Arkansas titanium deposits in Hot Spring County produced commercial-grade rutile concentrates from 1933 to 1942. These were sold mainly to England, Germany, and Russia.

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* Laboratory work for this report was completed Sept. 1, 1948. This paper presents the results of work done by the Rolla Branch, Metallurgical Division, of the Bureau of Mines.

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[1] References are at the end of the paper.

Table 1 . . . Matte Smelting of Ilmenite with Pyrite and Coke

Product	Weight, Pct	Analysis, Pct				Recovery, Pct	
		Ti	Fe	S	Total C	Ti	Fe
Matte	64.9	40.7	14.5	17.9	1.9	73.3	20.7
Metal	34.3	1.4	89.5	1.8	2.7	1.2	66.2
Fume	0.8	7.4	9.7	N.D.*		0.2	0.1
Dust losses						25.3	13.0
Total	100.0					100.0	100.0

* N.D. means not determined because of lack of sample.

The ore dressing of low-grade titanium ores containing approximately 4 pct TiO_2 to a high-grade concentrate of 92 to 95 pct TiO_2 places an unusual duty upon any ore-dressing plant. A high recovery of rutile under these conditions is sacrificed to produce a high-grade product. Examination of the tailings from any rutile mill of this type operating on mine-run ore in the United States will confirm this statement. One purpose of the laboratory work on the matte smelting of titanium is to be able to utilize lower-grade titanium concentrates and thereby directly facilitate the conservation of titanium minerals. There is no present commercial use of rutile concentrates containing less than 92 pct TiO_2. All of the laboratory work at Rolla on the matte smelting of titanium has dealt with a concentrate containing only 85 pct TiO_2. The ilmenite concentrates treated for matte smelting were of standard grade and of the following composition: 58.4 pct TiO_2, 25.0 pct Fe, 0.37 pct P_2O_5, 0.11 pct V_2O_5. It is necessary to mention that, in the production of ilmenite concentrates, the same general statement holds true in that considerable losses of ilmenite occur in the attempt to produce high-grade ilmenite mineral concentrates. The recent introduction of flotation for the recovery of fine ilmenite and rutile values has been of considerable assistance in improving these recoveries. The presence of clay minerals, however, interferes with the recovery of fine titanium minerals in flotation the same as in gravity concentration.

Preparation of Titanium Tetrachloride

GENERAL

Titanium tetrachloride is commonly prepared by one of the following processes: (1) Chlorination of titanium cyanonitride, which product is prepared from pigment-grade titanium dioxide or high-grade rutile concentrate in the electric arc furnace, (2) chlorination of pigment-grade titanium dioxide at 400 to 900°C, and (3) chlorination of ilmenite or rutile concentrates at 500 to 1100°C. Methods 1 and 2 suffer from the disadvantage of requiring a relatively expensive starting material; that is, pigment-grade titanium dioxide, which has recently been quoted at \$0.19 per ½ lb or high-grade rutile concentrates which cost approximately \$0.07 per lb.[4] Method 3 requires a comparatively high chlorination temperature.

Chlorine is an extremely active chemical reagent at elevated temperatures. None of the common metals or alloys is resistant to its action although certain acid-resisting refractory brick and graphite are not affected by chlorine at the reaction temperatures used. In laboratory tests made on the chlorination of ilmenite-carbon mixtures several types of graphite retorts, coated with the refractory cements available, were tried. All of the tests showed that graphite was unsatisfactory because of its porosity and because of its tendency to oxidize rapidly at temperatures above red heat. None of the coating materials adhered to the graphite tubes well enough to prevent them from being oxidized.

It is believed that it would be extremely advantageous to develop a process for producing titanium tetrachloride by chlorinating a titanium compound at a temperature less than 300°C. In perusing the literature it was found that one of the most likely compounds of titanium for this purpose was the sulphide. M. Picon[5] stated that all of the sulphides of titanium were attacked by chlorine at 175°C, titanium chloride being volatilized.

Little previous work has been done on the preparation of titanium sulphides. Some of the methods used were as follows: (1) Reaction between titanium tetrachloride vapor and hydrogen sulphide at 480 to 540°C,[6] (2) reaction between a mixture of titanium dioxide and graphite with dry hydrogen sulphide,[7] (3) reaction between carbon disulphide and hot titanium oxide,[8] and (4) reaction between mixtures of iron sulphide, titanium dioxide, and carbon.[9]

Of these methods (1) is obviously unsuitable since one of the starting materials is titanium tetrachloride. However, during the course of this research some pure titanium disulphide was made by this method in order to prepare a standard X ray diffraction pattern and to determine some of its fundamental characteristics. Of the remaining three methods, a variation of (4) appeared to be the most attractive.

PREPARATION OF TITANIUM MATTES

In January 1947 a study of the reactions between rutile, pyrite, and coke, and ilmenite, pyrite, and coke was started. In the preliminary tests 200-g samples, charged in a graphite crucible, were smelted in a 3 kv-amp. high-frequency induction furnace. All of the constituents were ground to minus 200-mesh. The purpose of this work was to produce a matte containing all of the titanium in the form of the sulphide, while the reduced iron was separated from the matte in a metallic button at the bottom of the crucible. This metal should be a useful by-product as molten feed to a bessemer converter.

To determine the proper conditions for recovering the maximum amount of the charged titanium in the matte and at the same time produce a desirable titanium sulphide product, the composition of the charges, the smelting temperature, and the time were varied.

In one series of experiments the composition of the charge was varied from 20 to 60 pct ilmenite and 30 to 70 pct pyrite, and the coke was held constant at 10 pct. The results of these experiments showed that, as the pyrite in the charge was increased, the percentage of titanium in the matte decreased and the percentage of iron increased. As the percentage of titanium in the matte increased, its solubility in 10 pct and concentrated sulphuric acid decreased. It is believed that this was caused by the formation of suboxides of titanium as the amount of pyrite in the charge was decreased.

In a typical run a 200-g charge, consisting of 60 pct ilmenite, 30 pct pyrite and 10 pct coke, was charged into the small induction furnace, heated to approximately 1500°C, and smelted for 45 min. at this temperature. After the smelting period the charge was allowed to cool in the crucible and the matte separated from the metal. The result of this run is shown in Table 1.

The results of these experiments were not entirely conclusive because of the large losses by "dusting" that occurred during the charging of the small induction furnace and during the reaction period. However, in larger-scale work when rutile was smelted with pyrite and coke, recoveries exceeding 90 pct of the titanium in the charge were obtained in the mattes. These initial experiments showed that it was possible to prepare titanium mattes by smelting mixtures of ilmenite, pyrite and coke at approximately 1550°C.

Several small-scale experiments were made in which mixtures of rutile, pyrite, and coke were smelted in the small induction furnace to determine whether there was any difference in the behavior of rutile in the matte smelting reaction as compared to ilmenite. No marked difference was found between the two minerals. However, rutile gave a distinctly less violent reaction than ilmenite, and the fusion temperature of the various mixes was somewhat higher. The rutile used in these and all of the following tests was an 85-pct TiO_2 mill concentrate which did not meet the specifications of commercial-grade rutile.

Little work has been done on identification of the various matte constituents and a large number of these remain to be identified. It is believed that some of the reactions which occur are as follows:

$$TiO_2 + 2C = TiO + CO$$

$$TiO_2 + FeS_2 + 2C = TiS_2 + Fe + 2CO$$

$$CO_2 + C = 2CO$$

$$4TiO_2 + 3FeS_2 + 8C = 2Ti_2S_3 + 3Fe + 8CO$$

$$TiO + TiS_2 = TiO \cdot TiS_2$$

$$TiO_2 + FeS_2 + 2C = TiFeS_2 + 2CO$$

$$2TiO_2 + C = Ti_2O_3 + CO$$

$$TiO_2 + 3C = TiC + 2CO$$

$$FeS_2 = FeS + S$$

$$2TiO_2 + 4C + 4FeS = 2TiS_2 + 4Fe + 4CO$$

$$2TiO_2 + 4C + 3FeS = Ti_2S_3 + 3Fe + 4CO$$

$$2TiO_2 + 4C + 2FeS = 2TiS + 4CO + 2Fe$$

X ray studies of the mattes are being made to determine the various constituents present in order to increase our knowledge of the reactions which occur during matte smelting.

CHLORINATION OF TITANIUM MATTES

In order to prepare a sufficiently large sample of titanium matte for chlorination experiments, several samples of matte were prepared in the 35 kv-amp. high-frequency induction furnace. This larger induction furnace was similar to the one previously described, except that the inside diameter of the graphite crucible was 3¾ in. as compared to 1¼ in. for the smaller furnace, and 1,500-g charges were smelted as compared to the 150- and 200-g charges melted in the smaller furnace.

In most of the experiments the charge was smelted for one hour at an approximate temperature of 1550°C, allowed to cool, and the matte separated from the metal. The charge compositions and chemical analyses of four typical mattes are shown in Table 2.

Table 2 . . . Matte Samples Used in Chlorination Experiments

Sample	Analysis, pct				Composition of Charge, Pct
	Ti	Fe	S	C	
1	44.6	9.4	19.7	2.2	55 pct rutile, 35 pct pyrite, and 10 pct coke.
2	37.2	14.8	27.2	2.5	45 pct rutile, 45 pct pyrite, and 10 pct coke.
3	31.6	22.8	31.2	3.7	35 pct rutile, 55 pct pyrite, and 10 pct coke.
4	37.3	19.3	28.1	1.5	45 pct rutile, 45 pct pyrite, and 10 pct coke.

After spending considerable time in devising suitable apparatus for carrying out the chlorination experiments, it was found that a stainless-steel retort containing 25 pct chromium and 12 pct nickel was most satisfactory. A collecting system was devised that consisted of a short length of 1½-in. stainless steel pipe welded to the retort which was in turn connected by means of a length of rubber tubing to a length of 1¼-in. glass tubing that extended into a 4-liter filter flask serving as a collecting vessel. The flask was connected in series to three 500-ml Erlenmeyer flasks, the first of which contained hydrochloric acid and the other two, water. The purpose of the first Erlenmeyer was to keep the system free of water vapor, and the other two were to remove the volatile titanium compounds in the exit gas. The retort was heated by a tube furnace held in a vertical position. The charge was supported on a carbon plug drilled with 1/16-in. holes, which in turn was held in position by means of the chlorine inlet tube which was flared at its end. A 1½-in. pipe cap was screwed on the bottom of the retort to make the apparatus air-tight, and the cap was drilled and tapped to permit the chlorine inlet tube to pass inside the retort.

In order to keep the charge, which was ground to minus 200-mesh, from falling through the carbon plug, it had to be mixed with a binder. In several of the earlier tests fuel oil was used as binder. However, it was later found that benzol was more suitable for the laboratory work as it volatilized at a lower temperature. In some of the earlier runs activated charcoal was mixed with the titanium matte in the charge; but, as it seemed to have little effect on the chlorination reaction, its use was discontinued.

The reaction time and temperature were varied considerably during the earlier experiments. Temperatures from room temperature to as high as 400°C and reaction periods from 1 to 4 hr were used. However, in later runs, a reaction temperature of 200 to 220°C and a reaction time of 4 hr were used. After chlorination, the residues were generally leached with water to remove any of the ferric chloride formed, so as to provide an analytical sample that was not hygroscopic.

The initial experiments showed that it was possible to recover 60 pct of the titanium in the mattes by chlorination, when the charge composition of the matte contained 45 pct or more pyrite. Additional tests were made to improve the titanium recovery from mattes containing 55 pct rutile, as it was obvious that it would be more economical to prepare a matte of higher titanium content. These later runs showed that recovery could be increased and are described later.

The product obtained by the chlorination of titanium mattes was a yellow, hygroscopic, crystalline solid which fumed when exposed to the atmosphere. During the course of the reaction an amber liquid was first recovered, which was converted to the yellow solid by further reaction. The chemical composition of this solid, as determined in some 5 or 6 dozen cases was as follows: Titanium 17–21 pct, sulphur 4–6 pct, chlorine 67–75 pct. It is believed that chlorination proceeded according to the following reactions:

1. $TiS_2 + 2Cl_2 = TiCl_4 + 2S$
2. $2S + Cl_2 = 2SCl$
3. $TiCl_4 + 4SCl = TiCl_4{\cdot}SCl_4 + 3S$

The product obtained from the various chlorination reactions was identified as a mixture of titanium tetrachloride and titanium sulpho-octochloride ($TiCl_4{\cdot}SCl_4$). It is apparent that this product must be treated further to remove the sulphur.

REMOVAL OF SULPHUR FROM CRUDE TITANIUM CHLORIDE

Several methods were tried for purifying the material obtained by the chlorination of titanium matte. Simple distillation was unsuccessful because titanium tetrachloride and sulphur monochloride have boiling points that are within 0.8°C of each other. A number of inorganic materials, that have an affinity for sulphur, were added to the crude titanium chloride, and the mixture was heated until distillation occurred. Some of the reagents used were sodium carbonate, sodium hydroxide, lime, aluminum powder, iron powder, and titanium wire and powder. None was satisfactory as the sulphur content of the product varied from 0.23 to 3.00 pct.

At the suggestion of O. C. Ralston, chief of the Metallurgical Division, Bureau of Mines, fixed oils, such as cottonseed oil, and fatty acids such as palmitic acid, coconut oil fatty acid, and oleic acid were mixed with the impure titanium tetrachloride and heated slowly for a short time until distillation occurred. The use of such an oil was to provide a material that could be chlorinated by the sulphur chloride present thus splitting the sulphur from the chlorine and forming elemental sulphur, which has a considerably higher boiling point than titanium tetrachloride.

These fatty acids and oils were more successful than the inorganic reagents which had been used previously. In several runs titanium tetrachloride with a sulphur content of as low as 0.02 pct was produced. The optimum amount of oil used was 4 pct of the weight of the crude titanium compound charged.

In a typical run in which the charge consisted of 50 g of impure titanium compound and 2 g of soya bean oil fatty acids, three distillates were obtained. The first distillate contained 1.74 pct sulphur and consisted of 9.9 pct of the titanium charged, the second contained 0.02 pct sulphur and consisted of 52.5 pct of the titanium charged, while the third contained 0.09 pct sulphur and consisted of 24.0 pct of the titanium charged. The residue contained 13.6 pct of the titanium charged. The distillates which were high in sulphur could be returned to the still for further treatment. It should also be possible to reduce the titanium losses in the residue so that it may be safely assumed that 90 pct or more of the titanium charged should be recovered.

Further work showed that it was possible to replace the fatty acids and oils with tall oil, a cheaper material obtained as a by-product in the manufacture of paper.

At present, nothing is known of the amount of sulphur that may be tolerated in the titanium tetrachloride used in the Kroll process. It may be possible to use a product that is less pure than has been previously described, which would naturally lower the operating cost and probably increase the titanium recovery.

USE OF SILICON IN MATTE SMELTING

All of the titanium mattes prepared thus far contained a certain amount of iron, probably in the form of suspended metallics and as iron sulphide. During chlorination a considerable amount of chlorine is used in producing ferric chloride, as iron is attacked before titanium. The commercial value of this byproduct has not been investigated. Several methods were tried to lower the iron content of the mattes. Various reagents, including sodium carbonate, lime, aluminum, copper, and electrolytic manganese were added to samples of matte in the molten condition. All of these reagents were ineffective. During a conference with Dr. William J. Kroll of the Albany, Oregon, Branch of the Bureau of Mines it was suggested by him that silicon be tried as a desulphurizer. It was believed that the silicon might react with the iron sulphide in the matte removing the sulphur in the form of volatile silicon sulphide thus forming metallic iron which would be collected in the metallic button.

Various methods of adding silicon to the charge were tried. One of the most effective ones appeared to be to smelt the batch of rutile, pyrite, and coke in the usual manner, hold it at the reaction temperature for 30 min. to one hour, then add the metallic silicon, stir the batch as thoroughly as possible and hold it for an additional shorter period, usually 15 to 30 min. at the reaction temperature, 1500 to 1550°C.

Many mattes were prepared in which silicon was added to the charge. The amount of silicon added was 2 to 4 pct of the weight of the charge. In general, the iron contents of the finished mattes were lower than those of corresponding mattes in which silicon was not used. However, all of the mattes contained some silicon, ranging from 0.11 to 8.7 pct, depending on the quantity of silicon added and the method of mixing it with the matte. In some instances, when the silicon was not thoroughly stirred into the matte it collected on the surface in the form of a slag.

Several of the silicon-containing mattes were chlorinated. In general, the titanium recoveries were somewhat higher when silicon was added to the matte. In one case, a titanium recovery in excess of 90 pct was obtained from a matte with a charge composition of 55 pct rutile, 35 pct pyrite, and 10 pct coke, to which silicon amounting to 2 pct of the original charge was added. In several other runs in which all of the experimental conditions of the previous test were duplicated, it was not possible to obtain a titanium recovery in excess of 70 pct. Apparently, this reaction of silicon with titanium matte is very sensitive and difficult to control. The function of silicon in the matte smelting reaction has not been ascertained. However, in most cases, the bulk of the silicon was not volatilized and remained in the matte, slag, and metal. Some of the metals had a silicon content of nearly 10 pct. More experimental work is necessary to determine the function

Table 3 . . . Matte Smelting in the Globar Furnace

Product	Weight, Pct	Analysis, Pct			Distribution of, Pct		
		Ti	Fe	S	Ti	Fe	S
Matte	79.7	48.5	8.6	19.6	97.0	30.4	96.2
Metal	18.0	2.0	86.4	2.7	0.9	68.9	3.0
Slag	2.3	36.2	6.6	5.6	2.1	0.7	0.8
Composite	100.0				100.0	100.0	100.0

of metallic silicon when introduced into molten titanium mattes.

SMELTING IN THE GLOBAR FURNACE

It was noted in the early work that an induction furnace was not entirely satisfactory for preparing titanium mattes because of its uneven heating caused by the difference in conductance of the metallics and the matte, and because of the dusting losses which occurred when the furnace was charged. The experiments made in the induction furnace, however, gave an indication of the results that might be obtained in larger-scale work.

A series of experiments was made in a globar furnace to approach more nearly the hearth-type furnace and determine its suitability for titanium matte smelting. The furnace used had a hearth that was 18 in. deep and 25 in. wide. The roof was arched, and it was 17½ in. high on each side and 18½ in. in the center. There was enough room to charge four crucibles. The samples were charged into deep graphite crucibles to make a better separation between metal, matte, and slag.

In all of the experiments the charge weights were varied from 2000 to 2400 g. In the initial runs the samples were charged at 1200°C, heated to 1550°C, and held at this temperature for one hour, the total furnacing time being 7 hr. In later runs the samples were charged at 1550°C and the total furnacing time was 4½ hr. In two of the runs in which silicon was added to the samples, the charge was held at 1550°C for one hour previous to the addition. After the silicon was added the charge was stirred and held at the reaction temperature for another 30 min. The total time the samples were in the furnace was 6 hr. In some of the experiments the samples were held at the reaction temperature for 30 min.

A typical run consisted of mixing a 2000-g charge containing 55 pct rutile, 35 pct pyrite, and 10 pct coke, charging into the globar furnace at 1100°C and heating for a period of 30 min. at 1550°C. The analyses of the matte, metal, and slag formed are shown in Table 3.

All of the mattes produced in the globar furnace were chlorinated under various experimental conditions. The reaction temperatures were varied from 200 to 300°C, while the time was held constant at 4 hr. The results of these experiments showed that in most cases the titanium recoveries obtained from samples made in the globar furnace were approximately the same as samples made in the induction furnace. The smelts made in the globar furnace, to which silicon had been added, showed that a considerable amount of the silicon was in the slag. This was probably caused by the difficulty of stirring these samples while they were being heated.

In runs in which the reaction time was reduced from one hour to ½ hr the titanium recovery was somewhat lower. In several of the samples in which the rutile was increased to more than 60 pct of the weight of the charge, the titanium recovery was markedly reduced when the sample was chlorinated. The titanium recoveries obtained by the chlorination of several mattes made in the globar furnace are shown in Table 4.

SMELTING IN THE ELECTRIC ARC FURNACE

In order to prepare larger samples of titanium matte than had been made previously and also to study the smelting of these mattes in an electric arc furnace, several charges were smelted in a 100 kv-amp. single phase series arc furnace which had a carbon hearth.

In one run a charge weighing 100 lb and consisting of 55 pct rutile, 35 pct pyrite, and 10 pct coke was smelted. When the charge became molten at 1550°C, 2 pct by weight of silicon was added. After the silicon was added, the bath was thoroughly rabbled, and then poured. The total time between charging and pouring was about 2 hr, and the current and voltage were 900 amp and 70 volts, respectively. The rutile charge seemed to be ideal for smelting in an arc furnace, and the electrode consumption was considered normal. The matte from the fusion contained 42.6 pct titanium, 24.3 pct sulphur, 10.9 pct iron, and 0.11 pct silicon.

A chlorination experiment made on a sample of this matte in which the initial temperature was 150°C, the reaction time 4 hr, and the average chlorine flow 204 cc per min., gave a titanium recovery of 81.3 pct and an iron recovery of 95.0 pct. This was approximately the same titanium recovery as obtained previously in smaller-scale runs made in the induction furnace in which metallic silicon was added to the matte.

Preparation of Titanium Oxide Pigments

GENERAL

During the past 20 years the use of titanium oxide pigments has increased tremendously. Since 1939 titanium dioxide has been utilized in greater quantity than any other white pigment.[10] Production and sales of titanium pigments established new high records in 1947, but the capacity production rate was inadequate by a substantial margin to fill the peak and still growing demand for the product. Because of its superior pigment properties it is reasonable to expect that the demand for titanium dioxide will continue to be strong.

During 1947, 473,154 tons of ilmenite, estimated to contain 248,231 tons of titanium dioxide, were used for making pigments in the United States.[11] As far as is known, no rutile was used. The reasons for this are the difficulty of extracting pigment-grade titania from rutile and the present higher cost of rutile concentrates, as compared to ilmenite. If our reserves of ilmenite should become depleted, it may become necessary to use rutile or other titanium minerals as a source of pigment-grade titanium dioxide some time in the future. The use of lower-grade rutile concentrates should lower the cost of producing titanium dioxide

Table 4 . . . Chlorination of Titanium Mattes Made in the Globar Furnace

Sample	Analysis, Pct				Charge Composition, Pct and Remarks	Recovery, Pct by Chlorination	
	Ti	Fe	S	C		Ti	Fe
5	33.5	26.0	31.4	2.8	35 rutile, 55 pyrite, 10 coke. Reaction time is 1 hr at 1550°C, total time in furnace is 7 hr.	65.8	82.9
6	48.5	8.6	19.6	2.4	55 rutile, 35 pyrite, 10 coke. Reaction time is 1 hr at 1550°C, total time in furnace is 7 hr.	63.7	90.4
7	39.5	17.1	22.8	3.1	49.4 rutile, 38.0 pyrite, 12.6 coke. Total time in furnace 4½ hr. Held at 1550°C for 1 hr.	66.0	88.5

Table 5 . . . Leaching Titanium Matte with Sulphuric Acid

Sample	Concentration		Recovery	
	Ti	Fe	Ti	Fe
Leach liquor	21.55 g per liter	13.94 g per liter	60.4	95.4
Residue	36.35 pct	1.74 pct	39.6	4.6
Composite	43.50 pct	17.80 pct	100.0	100.0

from this mineral.

In the earlier work it was shown that titanium mattes made from ilmenite were soluble in 10 pct and concentrated sulphuric acid solutions. A study of the solubility of titanium mattes made from ilmenite and rutile was undertaken to determine whether the mattes would be suitable starting materials for the production of titanium oxide pigments.

LEACHING WITH AQUEOUS HYDROCHLORIC AND SULPHURIC ACID SOLUTIONS

The usual method of extracting titanium from ilmenite is by digestion with concentrated sulphuric acid solutions at 150 to 180°C. Accordingly, in the initial runs the mattes were leached with sulphuric acid solutions of various concentrations. The leaching times and temperatures were varied. In a typical run a 50-g sample of matte made by smelting a mixture of 49.4 pct rutile, 38.0 pct pyrite, and 12.6 pct coke in the 35 kv-amp. induction furnace for one hour at 1600°C and containing 43.0 pct titanium, 16.1 pct iron, 20.2 pct sulphur, and 4.8 pct carbon was leached with 143.6 g of 97 pct sulphuric acid solution for a period of 4 hr at 160 to 180°C. The mixture, which was then quite viscous, was allowed to cool and agitated for an additional ½ hr with 300 ml of water at 60 to 80°C, filtered, and washed with 200 ml of water. The results of this run are shown in Table 5.

The results of the leaching experiments with sulphuric acid solutions showed that recoveries of 25 to 75 pct of the titanium in the mattes could be obtained, dependent on the reaction conditions. Higher titanium recoveries were obtained when higher leaching temperatures and more concentrated sulphuric acid solutions were used. Increasing the amount of sulphuric acid above a 10 pct excess had no effect on titanium recovery. Increasing the leaching time to a period greater than 4 hr gave slightly higher titanium recoveries. In several cases titanium mattes that were made from charges containing 35 pct or less rutile gave recoveries that were greater than 90 pct when leached with sulphuric acid solutions.

Several experiments were made in which hydrochloric acid solutions were used to leach some of the titanium mattes. Concentrations of 10 pct, 20.24 pct (constant boiling mixture), and 37 pct hydrochloric acid solutions were used. In no case was it possible to obtain a titanium recovery greater than 30 pct. This was considerably less than had been obtained with sulphuric acid solutions. It is believed that leaching with hydrochloric acid removed only the TiS and subsulphide contents of the mattes.

BAKING WITH SULPHURIC ACID

In the earlier experiments, it was found that, when the mattes were leached with sulphuric acid, increasing the temperature increased the titanium recovery. A series of experiments was made in which titanium mattes were baked with sulphuric acid at temperatures varying from 200 to 400°C. The amounts of sulphuric acid used, the reaction temperatures, and reaction times were varied. The general procedure was to mix the acid and matte, bake at the required temperature, allow to cool, leach with water, filter and wash the residue. The optimum experimental conditions were baking for 1 to 2 hr at a temperature of 200 to 250°C with a 100 pct stoichiometric excess of sulphuric acid. With these conditions it was possible to recover 90 to 95 pct of the titanium from mattes of high titanium content (40–50 pct titanium). Baking these mattes with sulphuric acid increased the titanium recoveries from 15 to 25 pct as compared to similar experiments in which they were leached with aqueous sulphuric acid solutions. It is believed that the higher temperatures used in the baking experiments put the suboxides of titanium into solution.

In a typical run a 50-g sample of matte made from a batch consisting of 55 pct rutile, 35 pct pyrite and 10 pct coke, and containing 42.8 pct titanium, 9.2 pct iron, 20.2 pct sulphur, and 1.78 pct carbon was mixed with 205.5 g of concentrated sulphuric acid and heated for 2 hr at 225 to 250°C. The sample was allowed to cool, leached with 300 ml of water, filtered and the residue washed with 200 ml of water. The result of this run is shown in Table 6.

There are several advantages in treating titanium matte, as compared to ilmenite. For one, the quantity of iron in the matte is considerably lower than in ilmenite, thus reducing the amount of ferrous sulphate in the leach solution. The leach solutions obtained from high titanium mattes contained one-sixth to one-eighth the amount of iron as compared to similar solutions from ilmenite. This will simplify the purification process by reducing the amount of ferrous sulphate to be handled. Another advantage is the fact that the matte has a higher titanium content than ilmenite thus reducing the handling cost. Although considerable acid (100 pct stoichiometric excess) is necessary in most cases for a maximum titanium recovery, a large amount of this acid can be recovered in the form of sulphur trioxide and elemental sulphur.

It has been shown that titanium recoveries in excess of 95 pct can be obtained by baking titanium mattes with sulphuric acid at 200 to 250°C. Very little work has been done, however, on the precipitation of titanium dioxide or the adjustment of the concentration of the leach solution. It is believed that a countercurrent decantation system

Table 6 . . . Baking Titanium Matte with Sulphuric Acid

Sample	Concentration		Recovery	
	Ti	Fe	Ti	Fe
Leach liquor	37.6 g per liter	8.6 g per liter	98.6	99.0
Residue	2.6 pct	0.44 pct	1.4	1.0
Composite	45.0 pct	10.24 pct	100.0	100.0

of leaching can be developed for leaching the baked matte. A sulphur balance must also be made to determine the amount that may be recovered from the system.

BAKING CHLORINATION RESIDUES WITH SULPHURIC ACID

The residues from the various chlorination tests contained 30 to 60 pct of the titanium in the original mattes and analyzed 25 to 35 pct titanium. Several runs were made on samples of these residues obtained from the chlorination of mattes prepared in the electric arc, induction, and globar furnaces. The procedure used was similar to that described in the previous section and consisted of baking the chlorination residue with sulphuric acid followed by a water leach. In all cases titanium recoveries over 90 pct were obtained. The arc-furnace product gave a recovery of 98.4 pct, the induction furnace product gave 90.6 pct, and the globar furnace gave 94.7 pct.

In Table 7 are shown the chemical analyses and over-all distribution of titanium in the various products obtained by chlorination and sulphuric acid baking of a sample of titanium matte prepared in the electric arc furnace.

A recovery of 95.2 pct of the titanium in the rutile concentrate has been obtained in usable form. It is also believed that a major part of the titanium in the slag may be recovered by sulphuric acid leaching or baking.

Preparation of Titanium Sulphides by Reaction of Rutile with Carbon Disulphide Vapor

Several experiments were made to determine whether titanium sulphides could be economically prepared from rutile by reaction with carbon disulphide vapor at elevated temperatures. In these tests, 85 pct rutile concentrates and a sample of low-grade rutile middling were sulphidized. Work on the low-grade material was abandoned when it was found that the gangue mineral, ankerite ($CaO\cdot(MgFe)0.2CO_2$) was sulphidized before the rutile, thus causing an excessive consumption of carbon disulphide.

The procedure and apparatus used in these experiments were as follows: A weighed sample was mixed with a binder and charged into a vertical tube furnace. The charge was supported on a carbon block which was drilled with $\frac{1}{16}$-in. holes to permit the carbon disulphide vapors to pass through the sample. The alundum or fused-silica tube was heated by an electric resistance furnace controlled by a rheostat. A weighed sample of carbon disulphide was placed in a three-necked Pyrex flask and heated by a water bath. A current of helium gas was passed over the surface of the carbon disulphide to carry it through the charge. The gases issuing from the top of the retort were passed through a water-cooled condenser to condense any unreacted carbon disulphide. The carbon disulphide was collected in a separatory funnel and returned to the distillation flask, while the tail gases were bubbled through a water trap to the atmosphere.

In a typical run a 150-g sample of 85 pct rutile was mixed with 7.9 g of sawdust and 29 g of water and heated to 800°C for 15 min. to remove the water and the volatiles in the sawdust. The charge was then heated at 1100°C for 8 hr while carbon disulphide vapor was passed through it. During the run 272 g of carbon disulphide were used. Part of this was used to sulphidize the rutile while the remainder was decomposed to form carbon and elemental sulphur. The analysis of the product obtained was 42.2 pct titanium, 26.4 pct combined sulphur, 2.4 pct free sulphur, and 0.54 pct carbon.

Table 7 . . . Over-all Distribution of Titanium in Products from Titanium Matte

Sample	Concentration				Titanium Recovery
	Ti	Fe	S, Pct	Cl, Pct	
Chlorination product	17.8 pct	0.71 pct	5.8	78.4	63.6
Leach liquor from sulphuric acid bake	34.5 g per liter	1.6 g per liter			31.6
Leach residue	4.4 pct	0.9 pct	4.7		0.5
Metallic product obtained during matte smelting	0.33 pct	85.9 pct	1.2		0.1
Slag from matte smelting	39.8 pct	3.7 pct	18.8		4.2
Total					100.0

A 100-g sample of this sulphidized product was chlorinated for 4½ hr at 200 to 220°C. A recovery of 59.4 pct of the titanium in the rutile was obtained. The product contained 15.3 pct titanium, 0.5 pct iron, 7.8 pct sulphur, and 78.1 pct chlorine.

It is believed that a higher recovery of titanium may be obtained, but this will be at the expense of greater carbon disulphide consumption and longer reaction times.

Conclusions

The results of the laboratory research work done thus far indicate that it is possible to produce titanium tetrachloride and titanium oxide from rutile by means of smelting the rutile with pyrite and coke and then processing the titanium matte. An impure iron is recovered as a byproduct. Ilmenite may be treated in the same way as rutile.

Recoveries of from 65 to 81 pct of the titanium in rutile may be obtained as an impure titanium tetrachloride by chlorinating titanium mattes at 150 to 250°C. When titanium matte is baked with sulphuric acid at 200 to 250°C, recoveries of 90 pct or more of the titanium in the rutile are obtained in the form of a titanium sulphate solution which is suitable for the recovery of pigment-grade titanium dioxide.

Chlorinating the mattes, followed by baking the residues with sulphuric acid gave titanium recoveries greater than 90 pct.

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Recovery of Zinc by the Dithionate Sulphur-dioxide Leaching Process

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When manganese ores are leached with sulphur dioxide, a large part of any zinc in the ore usually is extracted with the manganese.[1] In the dithionate process,[2,3] in which the manganese ore is leached with dilute sulphur dioxide gas and the manganese is subsequently precipitated by adding lime to the pregnant solution, the zinc is precipitated with the manganese. These facts suggested the possibility of applying the dithionate process to the recovery of zinc from oxidized ores or calcined sulphide concentrates. Accordingly, an investigation was begun, and preliminary tests were made on several ores and concentrates. The results were encouraging, but the need to devote available funds and personnel to other projects made it necessary to drop the work before the various factors involved in the process could be studied in detail. A brief mention of the process,[4] however, elicited a number of inquiries, so that it appeared desirable to report the results of the preliminary work.

The dithionate process as applied to zinc may be summarized briefly as follows: The ore or calcined concentrate is leached with dilute SO_2 gas to dissolve the zinc, largely as zinc sulphate, in accordance with the following equation in which [ZnO] represents the "oxide zinc" in the ore or calcine:

$$[ZnO] + SO_2(g) + \frac{1}{2}O_2 = Zn^{++}SO_4^{--} \quad [1]$$

If, in the leaching step, the ore or calcine is suspended in calcium dithionate solution, the sulphate ion, as it is formed, is precipitated immediately as calcium sulphate, which is subsequently filtered off with the insoluble ore residue:

$$Zn^{++}SO_4^{--} + Ca^{++}S_2O_6^{--} = CaSO_4(s) + Zn^{++}S_2O_6^{--} \quad [2]$$

An alternative procedure is to suspend the ore in water, filter off the insoluble ore residue after leaching, add calcium dithionate to the resulting zinc sulphate solution, and then filter off the calcium sulphate precipitate. In either event the zinc is obtained in the form of a pregnant solution of zinc dithionate, from which it can be precipitated as relatively pure zinc hydroxide by adding milk of lime:

$$Zn^{++}S_2O_6^{--} + Ca(OH)_2 = Zn(OH)_2(s) + Ca^{++}S_2O_6^{--} \quad [3]$$

The zinc hydroxide precipitate is calcined to form the final zinc oxide product:

$$Zn(OH)_2 = ZnO(s) + H_2O(g) \quad [4]$$

Theoretically the process is completely cyclic with respect to dithionate ion, the calcium dithionate required for reaction 2 being replaced by that formed in reaction 3. In practice, of course, small amounts of dithionate would be lost in the various filter cakes, depending on the economic washing limits. In the leaching step, however, some of the SO_2 is oxidized to dithionate instead of sulphate, according to the following overall reaction:

$$ZnO + 2SO_2(g) + \frac{1}{2}O_2(g) = Zn^{++}S_2O_6^{--}, \quad [5]$$

so that the dithionate losses are made up, at least in part.

Ores and Concentrates Tested

The analyses of the ores and concentrates tested are summarized in Table 1, which also includes the analyses of the calcines produced from the concentrates. The concentrates were roasted in a laboratory muffle furnace at the temperatures indicated until evolution of SO_2 could no longer be detected; shallow clay dishes ordinarily were used; but calcines 2*a* and 2*c* were prepared in iron dishes, with the result that these two calcines were badly contaminated with iron scale.

The "complex" concentrate, sample 1, consisted essentially of sphalerite grains containing inclusions of pyrite and other sulphide minerals too minute to be liberated by grinding within economic limits. In the "marmatitic" concentrate, sample 2, the iron was present largely as marmatite (that is, as iron sulphide in solid solution in zinc sulphide) rather than as pyrite inclusions. The zinc was present largely as the carbonate in the two "oxidized" ores, samples 3 and 4, and as the silicate in the "willemite" ore, sample 5.

Leaching Tests

The leaching cell was a 3-liter glass beaker placed in an electrically heated water bath manually controlled to maintain a temperature of 35°C in the leach slurry. The slurry was agitated by means of a flat paddle-type stirrer

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[1] References are at the end of the paper.

rotating near the bottom of the cell at about 500 rpm. A mixture of SO_2 and air, containing approximately 3.5 pct SO_2 to simulate waste smelter gas, was introduced at a constant rate through two 1-mm glass orifices, the gas emerging in the direction of rotation of the stirrer at a point near the periphery of the cell about an inch above the bottom.

The material to be leached was suspended in water. In each test a quantity of minus 65-mesh ore or calcined concentrate containing approximately 50 g of zinc was placed in the cell, 1500 ml of water was added, the stirrer was turned on, and the 3.5-pct SO_2 gas was introduced at the rate of approximately 36 g per hr for the desired length of time, usually 6 hr. At the end of the leach the slurry was filtered, the residue was washed, and the products were analyzed. The results of various leaching tests are given in Table 2.

Table 1 . . . Analyses of Ores, Concentrates, and Calcines

Sample No.	Sample	Analysis, Pct or Ounces per Ton								Oxide Zn, Pct of Total Zn
		Zn	Total S	Sulphide S	Fe	Pb	Cu	Au	Ag	
1	Complex concentrate	38.8	34.2		13.3	2.5	1.5	0.08	6.0	
1*a*	Calcine, 985°C	46.0	2.0	0.7	16.4	2.5	1.8	0.10	6.0	
1*b*	Calcine, 1035°C	48.4	1.1	1.0	19.2	3.0	1.9	0.12	9.5	
1*c*	Calcine, 1000°C	50.7	1.2	0.1	16.5		2.0	0.12	8.0	80.0
1*d*	Calcine, 800°C	43.8	5.8		14.8	2.6	1.7	0.10	6.2	82.7
2	Marmatitic concentrate	46.1	30.8		12.4	1.8	0.6	0.24	3.5	
2*a*	Calcine, 940°C	43.2	0.3		26.3		0.6	0.23	2.9	71.0
2*b*	Calcine, 600°C	48.9	4.7	0.3						84.8
2*c*	Calcine, 600°C	42.8	8.8	0.2						85.8
3	Goodsprings oxidized ore	24.4	0.3		4.2	10.3	0.7	Tr	3.2	
4	Leadville oxidized ore	25.4	0.1		14.2	0.1	<.1			
5	Willemite ore*	47.2			4.7	0.7	0.4			

* SiO_2, 22.2 pct.

Table 2 . . . Results of Leaching Tests

Leach No.	Sample Leached		SO_2 Introduced, Gram per Gram Zn	Extraction, Pct			S_2O_6 Formed, Lb per Ton Ore or Calcine
	No.	Description		Zn	Fe	Cu	
1	1*a*	Complex concentrate 985° calcine	4.3	83.2	2.8	44	61
2	1*b*	1035° calcine	2.1	60.4	0.3	1	30
3	1*b*	1035° calcine	4.3	82.4	1.2	34	46
4	1*c*	1000° calcine	4.1	80.0	1.0	33	77
5	1*d*	800° calcine	4.7	82.8	1.4	57	42
6	2*a*	Marmatitic concentrate 940° calcine	4.4	73.9	1.8	22	43
7	2*b*	600° calcine	4.3	86.8			36
8	2*c*	600° calcine	4.3	86.1	2.8		19
9	3	Goodsprings ore	4.7	84.8	3.2	66	21
10	4	Leadville ore	0.7	37.1	0.2		61
11	4	Leadville ore	1.4	49.8	1.7		70
12	4	Leadville ore	2.1	54.6	0.1		66
13	4	Leadville ore	2.9	67.7	1.9		70
14	4	Leadville ore	4.3	72.2	2.1		77
15	5	Willemite ore	2.7	61.0	6.2		24

With 4.1 to 4.7 g of SO_2 per gram of zinc, 83 to 87 pct of the zinc was extracted from the calcined concentrates and from the Goodsprings ore; under similar conditions, 72 pct was extracted from the Leadville ore. Utilization of SO_2 was rather poor, since theoretically approximately 1.0 g of SO_2 would be required per gram of zinc to form zinc sulphate or sulphite and 2.0 g would be required to form zinc dithionate. The two tests on calcine 1*b* and the five on the Leadville ore indicate that SO_2 utilization becomes poorer as leaching progresses. The willemite ore gave an extraction of 61 pct with 2.7 g of SO_2 per gram of zinc, and it is probable that higher extraction would have been obtained with more SO_2. Extraction of silica from the willemite ore was 52 pct; the leach slurry filtered fairly well, but the filtrate sample, when examined some 46 days later, was found to have gelled. The calcine and Leadville ore slurries filtered rapidly, but the Goodsprings ore slurry filtered very slowly.

Extraction of zinc from the calcined concentrates agreed well with the percentage of zinc present as oxide, as determined by solubility in strong ammonium chloride-ammonium hydroxide solution; leaching tests with dilute sulphuric acid likewise gave approximately the same results. Microscopic, chemical, and X ray diffusion tests showed that virtually all the zinc in the leach residues was present as sulphide and ferrite, mostly the latter. Effect of ferrite formation is evident in tests 6, 7, and 8 of Table 2; when the concentrate was roasted at 940°C, zinc extraction was 74 pct, whereas when the concentrate was roasted at only 600° to minimize ferrite formation, the extraction increased to more than 86 pct.

Extraction of iron was very low, amounting to less than 3 pct in most of the tests. Copper extraction, which was erratic, apparently depends on the extent of leaching and on the conditions of roasting. No lead and less than 3 pct of the gold or silver was extracted.

Dithionate formation ranged from 19 to 77 lb S_2O_6 per ton of ore or calcine (0.03 to 0.10 g per gram of zinc extracted). This would be ample, in most instances, to make up for washing losses in the process, which, it is estimated, would not exceed 30 lb per ton in practice. In the manganese investigation,[2,3] however, it was found that dithionate formation depends on many factors, including size and shape of leaching tank, agitation rate, leaching rate, and method of introducing the gas, so that pilot plant tests would probably be required to determine whether dithionate formation would be adequate in leaching zinc ores or calcines under plant conditions. Dithionate formation was fairly constant in leaches 10 to 14, in which the leaching time ranged from 1 to 6 hr, indicating that most of the dithionate was formed during the first hour.

The ore and calcine samples lost a large part of their weight during leaching, so that the residues were substantially enriched in iron, lead, gold, and silver, as shown in Table 3, in which data for several typical tests are summarized. Compared with the original concentrate or ore, the increase in the iron, lead, gold, and silver assays was about threefold for the two concentrates and about twofold for the Goodsprings ore. The large losses in weight on leaching were due to the fact that the samples leached were suspended in water rather than in calcium dithionate solution; if the samples had been suspended in calcium dithionate solution, the leach residues would have contained considerable calcium sulphate formed by reaction 2, and the weight losses would have been much less.

Recovery of Zinc from Solution

Leach solutions for investigating the recovery of zinc oxide products were prepared from (A) the "complex" concentrate calcined at 600°C, (B) the "marmatitic" concentrate calcined at

Table 3 . . . Data on Leach Residues

Leach No.	Sample Leached	Residue Weight, Pct of Ore or Calcine	Residue Assay, Pct or Oz per Ton				
			Zn	Fe	Pb	Au	Ag
1	Complex concentrate						
	Calcine 1*a*	40.2	20.0	38.3	6.0	0.21	14.2
3	Calcine 1*b*	43.4	19.2	42.0			
5	Calcine 1*d*	36.8	21.1	38.4		0.26	16.1
8	Marmatitic concentrate						
	Calcine 2*c*	29.9	19.6	36.3			
9	Goodsprings ore	53.6	7.0	7.5	19.1		5.8
14	Leadville ore	61.5	11.7	23.3			

Table 4 . . . Results of Precipitation Tests

Test	pH	Analysis, Pct or Grams per Liter							Zn Distribution, Pct
		Zn	Fe	Ca	SO_4	S_2O_6	S	L.O.I.*	
Leach Solution									
A	3.4	43.8	1.0	2.5	62.0	1.2			100.0
B	3.1	48.8	0.7		51.2	1.4			100 0
C	3.7	27.6	0.3	0.7	36.4	1.0			100.0
$CaSO_4$ Precipitate									
A		0.1		27.5	66.2				0.2
B		2.1		26.0	64.5				3.7
C		0.05		26.5	63.8				0.1
Pregnant Solution									
A		39.8		15.0	5.9	172			99.8†
B		43.8		13.6	11.4	154			96.3†
C		27.0		15.7	1.9	146			99.9†
Zinc Precipitate									
A		54.0	1.3	2.4			5.9	21.2	99.8
B-1		20.5		1.4	3.9		19.8		9.5
B-2		52.6	0.8	7.9			6.8	14.8	86.8
C		56.4	0.6	2.8			3.3	16.8	99.9
Zinc Calcine									
A		68.6	1.6	3.0			1.7		99.8
B-2		61.6	0.9	9.3			4.7		86.8
C		67.2	0.7	3.3			1.6		99.9
Barren Solution									
A	7.4	<0.02		27.1	1.1	121			<0.1
B	10.5	<0.02		19.5	1.2	84.6			<0.1
C	9.8	<0.02		22.0	0.8	97.5			<0.1

* Loss on ignition at 1000°C.
† Includes zinc in wash solutions.

600°, and (C) the Goodsprings ore. A 200- to 300-g sample of each material was leached in 1500 ml of water with 3.5-pct SO_2 gas for about 12 hr, the residue was filtered off and the filtrate was treated as described below to precipitate calcium sulphate and zinc hydroxide successively. Each residue or precipitate was washed thoroughly, but to avoid dilution of the various solutions, the wash filtrates were discarded. The SO_2 contents of the solutions were not determined, but the odor of SO_2 was noticeable in the leach solutions and pregnant solutions, especially those from test B.

PRECIPITATION OF CALCIUM SULPHATE

To precipitate sulphate, leach solutions A and B were treated directly with finely divided crystals of $CaS_2O_6 \cdot 4H_2O$ assaying 13.3 pct Ca, 57.8 pct S_2O_6, and 0.35 pct SO_4 (theoretical analysis: 14.7 pct Ca, 58.8 pct S_2O_6) Before adding the dithionate crystals to solution C, however, the solution was first treated with small additions of 20-pct sulphuric acid solution until the odor of SO_2 could no longer be detected and the pH remained constant at 1.9; 6.0 g of H_2SO_4 was required per liter of the solution. The quantities of calcium dithionate used per liter of leach solution were as follows:

	$CaS_2O_6 \cdot 4H_2O$ Crystals Added Grams per Liter of Solution
A	309
B	273
C	253

The analyses of the precipitates (dried at 110°C) and of the pregnant solutions are given in Table 4; the dried precipitates correspond closely to $CaSO_4 \cdot \frac{1}{2} H_2O$, for which the theoretical analysis is 27.8 pct Ca and 66.1 pct SO_4.

PRECIPITATION OF ZINC

Freshly calcined lime containing 93.0 pct available CaO was used to precipitate the zinc. The lime was slaked in about 10 times its weight of water, and the milk of lime was added dropwise to the vigorously agitated pregnant solution over a period of about 45 min. Agitation was continued for several hours, after which the slurry was allowed to stand overnight, during which time the pH rose about two units. With pregnant solution B, sufficient lime was added to give a pH of 3.9, the resulting precipitate was filtered off, and the addition of lime was then continued as described. Theoretically 0.84 g of CaO is required to precipitate 1.0 g of zinc; the quantities actually used were as follows:

	pH	Available CaO Used, Grams per Gram Zn
A	7.4	0.83
B—First ppt.	3.9	0.10} 0.94
Final ppt.	10.5	0.84}
C	9.8	0.92

The precipitates were dried at 110°C, and portions of the final precipitates were calcined at 1000°C. The analyses of the precipitates, calcines, and barren solutions are summarized in Table 4.

The results show that virtually all the zinc in the leach solutions can be recovered as a calcine assaying nearly 70 pct Zn. No advantage appears to have been gained by acidifying the leach solution in test C. The double precipitation with lime in test B was detrimental, causing a loss of 9.5 pct of the zinc in the first precipitate. The lower grade of the product in test B compared with the other tests is due to the presence of considerable calcium sulphate as a result of the relatively high sulphate content of the corresponding pregnant solution. The reason for the differences in sulphate content of the pregnant solutions is not clear, however, since the three pregnant solutions have nearly the same calcium content. It may be that the solubility of calcium sulphate in the solutions varies with the sulphite content; pregnant solution B, which had the highest sulphate content, was known to be particularly high in sulphite, whereas pregnant solution C, which was lowest in sulphate, probably had the lowest sulphite content as a result of the acidification.

Discussion of Results

The dithionate process for zinc is similar in certain respects to two processes investigated by Lyon and Ralston. In one of these,[5] oxide ore or calcine is leached with sulphurous acid solution to dissolve the zinc as the hydrosulphite, the pulp is filtered, and the zinc is precipitated as the sulphite by either boiling the solution or adding zinc oxide. The precipitate is calcined to form zinc oxide and regenerate the sulphur dioxide. The reactions are as follows:

$$[ZnO] + 2SO_2 + H_2O = Zn(HSO_3)_2 \quad [6]$$

$$Zn(HSO_3)_2 + \text{heat} = ZnSO_3 + SO_2 + H_2O \quad [7a]$$

$$\text{or } Zn(HSO_3)_2 + ZnO = 2ZnSO_3 + H_2O \quad [7b]$$

$$ZnSO_3 = ZnO + SO_2 \quad [8]$$

Lyon and Ralston tested several ores and calcines and obtained high extractions of zinc in solutions containing 0.2 to 4 pct SO_2. Precipitation of the zinc by boiling or by adding zinc oxide was incomplete, however, owing to the rapid air oxidation of zinc bisulphite to zinc sulphate and, in the case of calcines, to the presence of zinc sulphate formed in roasting.

In another process investigated by Lyon and Ralston,[6] the zinc is extracted by leaching with sulphuric acid or by roasting with sulphuric acid and leaching with water. The zinc is then recovered from the zinc sulphate solution by a procedure similar to that in the dithionate process except that calcium chloride is used instead of calcium dithionate; that is, the solution is treated with calcium chloride to precipitate calcium sulphate and form zinc chloride solution, and the latter is treated with milk of lime to precipitate zinc hydroxide and regenerate the calcium chloride. Lyon and Ralston obtained precipitates assaying about 50 pct Zn, and calcination of the precipitates gave zinc oxide products assaying over 65 pct Zn. The main objection to the process, aside from the high acid consumption in leaching, was the fact that the treatment of the zinc chloride solution with lime resulted in the precipitation of basic zinc chloride rather than zinc hydroxide, so that the precipitates contained 6 to 10 pct chlorine. This would involve a loss (in addition to normal washing losses) of 240 to 400 lb of chlorine per ton of zinc precipitated and would require 375 to 625 lb of make-up $CaCl_2$ per ton of zinc. Moreover, about 6 pct of the zinc was volatilized when the precipitates were calcined; this zinc would be lost unless expensive fume-collecting equipment were provided to recover it.

The present preliminary investigation of the dithionate process indicates that it may have promise for the treatment of oxidized zinc ores that cannot now be treated commercially and of off-grade complex zinc sulphide concentrates that can now be marketed with only relatively poor return for the values contained. Its advantages include (1) utilization of waste SO_2 gas for leaching; (2) possibility of forming enough dithionate during leaching to make up for losses; (3) separation of zinc from lead, gold, and silver; (4) recovery of zinc from solution by a simple precipitation with lime; and (5) production of a zinc oxide product assaying nearly 70 pct Zn. To determine the commercial feasibility of the process, however, would require a more extensive investigation. Among the factors that should be studied are effect of SO_2 concentration in the gas and of type of leaching cell on zinc extraction, SO_2 utilization, and dithionate formation; relative merits of leaching in water versus leaching in calcium dithionate solution; and effect of sulphite in the leach solution on the precipitation of calcium sulphate.

Summary

1. A new dithionate process for treating oxidized zinc ores or low-grade zinc concentrates is described. The ore or calcined concentrate is leached with dilute SO_2 gas, sulphate is precipitated by means of cyclic calcium dithionate, and the zinc is recovered from the solution by precipitation with milk of lime.

2. In laboratory tests on several ores and calcined concentrates, 83 to 87 pct of the zinc was extracted, together with less than 3 pct of the iron, gold, or silver and none of the lead. Enough dithionate was formed during the leaching process to make up for losses. About 5 lb of sulphur dioxide was used per pound of zinc extracted.

3. Virtually all the zinc in the leach solution was recovered as a precipitate which, after being calcined, assayed nearly 70 pct Zn.

Acknowledgments

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Seminar on the Kinetics of Sintering

(With Discussion)

A. J. SHALER,* Member AIME

Introduction

The subject of the mechanism of sintering has received much attention in the past few years, particularly since the beginning of the series of AIME seminars in powder metallurgy of which this paper introduces the fourth. In the first of these, F. N. Rhines[1] brought together and discussed the available experimental data on the sintering of pure metallic powder, and succeeded in bringing to a sharp focus the attention of workers in this field on the established observations which a satisfactory theory must explain.

Several other authors[3,5,6] have, in the last few years, studied the phenomena that occur when cold metallic powders, loose or in the form of compacts, are first brought to elevated temperatures. Some workers[7] in the field of friction have recently studied the adhesion of solid metal surfaces when they are brought into close contact. These researches have indicated that several separate mechanisms operate simultaneously, at least during the first part of the sintering process. Some of them have been called *transient mechanisms*[4] because they are in general not absolutely necessary to sintering. Powders may be so prepared and so treated that these transient phenomena do not take place during subsequent sintering. This does not mean, of course, that their industrial and scientific importance is any less than that of the *steady-state* phenomena. The latter are changes that go on during sintering no matter how the powders are made or treated; they cannot be divorced from sintering.

One way to analyze the process of sintering into its component parts is perhaps to distinguish between these transient and steady-state phenomena. Some of the transient phenomena have been studied in the past few years. Hüttig[3] has shown that, when the temperature of metallic powder is slowly raised, the following events generally occur in order: (1) physically adsorbed gases are desorbed; (2) there is an atomic rearrangement of the surface, a sort of two-dimensional "surface-recrystallization"; (3) there is a breakdown of chemically adsorbed surface compounds; (4) there is a recrystallization in the volume of the metal. All these changes are shown by Hüttig and his coworkers to be completed fairly rapidly at lower temperatures than those generally used in sintering and are therefore not a part of the mechanism whereby the density of a mass of powder continues to change after long heating at an elevated temperature. But the first and third of these changes release gases in quantities which may or may not help to control the steady-state mechanisms, depending on when the voids become isolated from the outside of the compact.

Among the phenomena studied by Steinberg and Wulff,[8] there is the effect on sintering of residual stresses arising from the pressing operation. They found that the lateral surfaces of a green compact of iron are under a longitudinal residual tension-stress of the order of magnitude of half the yield-point for solid iron. If the outside surface is in tension, the core must be under longitudinal compression. When the compact is heated, the surface residual stress is thermally relieved first, and the compact therefore initially expands in the direction of its axis. This is a transient phenomenon, if for no other reason than the possibility of sintering unpressed powders, as demonstrated by Delisle,[9] Libsch, Volterra and Wulff[10] and others.[1]

The subject of recrystallization is dealt with further in a separate section, in view of its prominent place in sintering literature. It, too, is one of these transient phenomena.

Among the steady-state parts there may be distinguished the attraction between particles and its consequences, the spheroidization of voids in the compacts, and the densification or swelling of the compact.

There is considerable evidence[4,7] showing that cold metallic surfaces, when brought to within a few interatomic distances of one another, are attracted to each other by forces of the order of many thousands of pounds per square inch. A calculation, discussed in greater detail in another section, shows that this force changes but slightly when the temperature of the surfaces approaches the melting point. Actual measurements of forces of adhesion of this magnitude have been made by Bradley[12] on some nonmetals, but none has yet been made on cold or hot metals. This force is of sufficient magnitude to cause some plastic deformation in powder compacts, as will be shown below.

A second force of steady-state nature is due to the surface tension, which probably has the same origin as the force of attraction between surfaces.[16,4] A paper by Udin, Shaler, and Wulff[13] gives the results of precise direct measurements of its value for solid copper. The demonstration of the tendency for the surface tension to shrink a pore was long ago given by Gibbs.[17] He showed that its effect on a curved surface between two phases is equivalent to a pressure perpendicular to that

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[1] References are at the end of the paper.

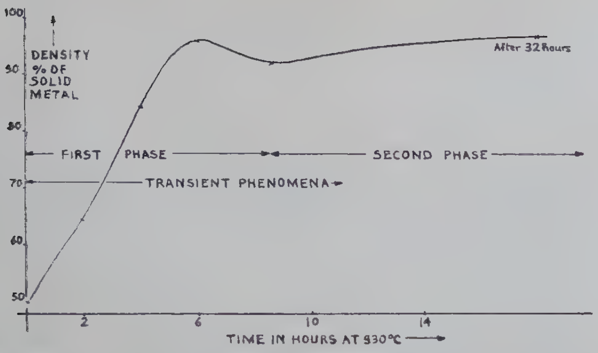


FIG 1—The progress of densification of a loose mass of copper powder (atomized #4915 MD63A, 5 pct 80 mesh, 10 pct under 150 mesh) in terms of per cent of the theoretical maximum.

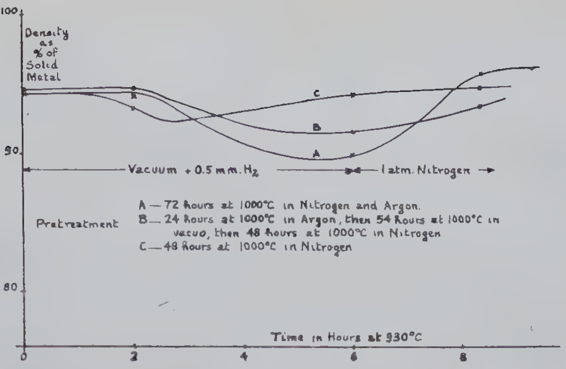


FIG 2—The progress of densification of compacts originally sintered in argon or nitrogen at one atmosphere, then subjected to heating variously in vacuo and in nitrogen.

surface and equal to twice the surface tension divided by the radius of the curvature. If the pressure of a gas within a pore is considered positive, then the pressure equivalent to the surface tension is a negative pressure directly opposed to it. Its magnitude depends on the size of the void. The interplay of this pressure and the pressure of the gases trapped within isolated voids has been described[18,28] elsewhere.

An attempt will be made in this paper to show that the ordinary modes of plastic deformation (slip and creep) contribute appreciably only in the first-stage of sintering to the change of density of a compact, and also that surface diffusion and evaporation cannot make major contributions to the process of densification (or swelling) in most metals. Another mode of flow must be demonstrated to exist in order to account for the changes in density of a compact during later stages of sintering. The nature of this flow is at present one of the major incompletely solved problems in the theory of sintering. This meeting will probably have heard, before its close, more than one version of how surface tension and gas-pressure-differences can cause densification or expansion of compacts. After a brief discussion of recrystallization and of the contribution to sintering of surface-diffusion and evaporation, the steady-state processes will be analyzed in more detail.

Recrystallization

The term "recrystallization" has been used in two different senses. In the first, it has been applied to the reorganization of the lattice following its distortion by cold deformation; it proceeds by the diffusion of individual atoms from the distorted lattice to a nucleus; the nucleus, if it is big enough, grows into a new crystal having (despite its more perfect geometry) a lower free energy. In the second, broader, sense of the term, recrystallization means any change in crystalline shape brought about by a movement of individual atoms. If sintering takes place by a diffusion of atoms and not by slipping or twinning of blocks of atoms, then it is certainly a recrystallization in this second sense; but the term is then no more specific than "sintering" itself, and its use gives no more insight into the nature of the phenomena.

Balshin[19] has advanced the hypothesis that recrystallization, presumably in the first, more restricted sense, begins at the points of contact between particles, where the greatest degree of cold deformation has been introduced during pressing, and that densification of the compact is a corollary of this recrystallization. But masses of powder need not be compressed in order to become more dense during heating. For illustration, Fig 1 shows the progress of densification of a mass of initially loose annealed copper powder (atomized, No. 4915 MD83A, Metals Disintegrating Co.) when it is heated in vacuo in a graphite container. According to this result, shrinkage does not require previous cold-working, and therefore requires no recrystallization. The converse, that recrystallization, in this sense of the word, does not result in shrinkage, can also be demonstrated. Smithells[20] reports that a cold-worked tungsten wire, coiled into an extremely fine coil, is recrystallized on heating in such a way that it becomes a single crystal whose orientation is independent of the direction of the axis of the wire, as if the coil had been machined out of a single crystal in the first place. No change in shape or size occurs during this recrystallization. In the same way, it is not to be expected that a composite of particles in contact with one another should change in shape or size even if the entire mass becomes recrystallized into a single, porous, crystal.

To demonstrate further that recrystallization following cold-work cannot be responsible for changes in the density of compacts, loose masses of powder were heated in argon or nitrogen at one atmosphere (14.7 psi) until their final stable equilibrium-density was reached (this equilibrium is described below). They were then heated in vacuo, wherein a different relation existed between the driving forces of surface tension and differential gas-pressure; they were observed to expand to a new equilibrium-density, which thereafter remained relatively stable in spite of further heating in vacuo. These compacts, as detailed in Fig 2, were then reheated again in nitrogen at one atmosphere until they regained their first equilibrium-density. It is highly improbable that these changes of external stress of 14.7 psi could induce enough deformation to initiate new recrystallizations. These experiments support the conclusion of Rhines[1] that recrystallization, in this sense, proceeds no differently in powder-compacts than in more massive metals, and have nothing to do with the changes in density of these compacts during sintering.

Such simple experiments further show that the reactions between the gases within the pores and the metal surrounding them have at most an influence on sintering which is independent of the main mechanism

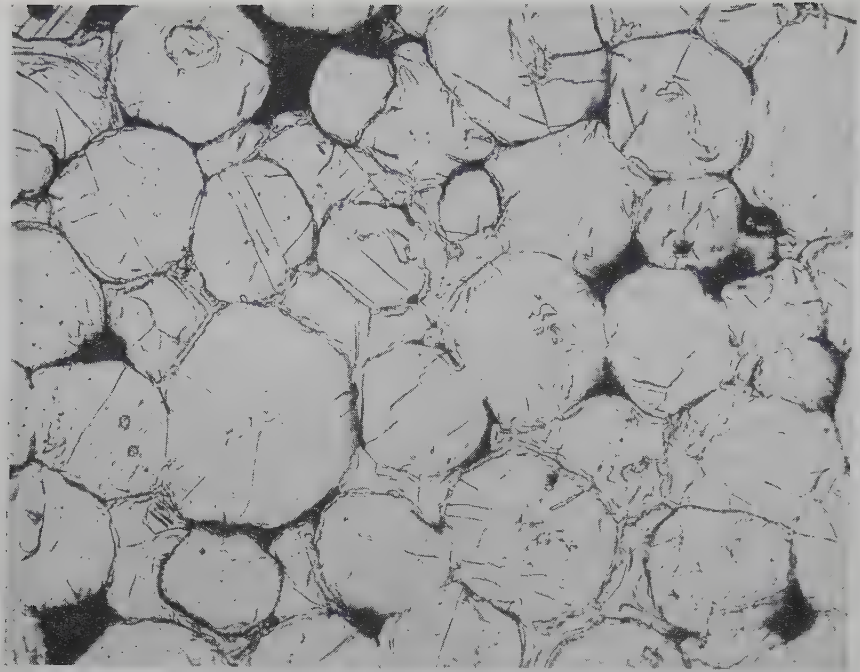


FIG 3—Micrograph at × 500 of loose copper powder heated 24 hr in argon at 1 atm at 1000°C, then 54 hr in vacuo at 1025°C.

Deeply etched and repolished several times. Density 97 pct of theoretical. Note tendency of pores to become spherical. Note also recrystallized "bridges" between some particles.

whereby compacts become more or less dense. A change in the pressure of gas outside the compact can in no way influence the equilibria of reactions at the surface of pores sealed from the outside, provided the temperature is not changed. The phenomena of recrystallization and of desorption or adsorption of gases are therefore of transient influence on sintering, and their effect is not in evidence after the first heating-up period, during which they govern the amount of gas that will be trapped within the pores. After that period, the nature of the sintering process must be sought in other phenomena.

Surface Diffusion and Evaporation

Pines[21] and more recently Ivensen[22] have stated that surface diffusion and the process of evaporation from one place and condensation at another cannot change the density of a compact. This thesis has been further supported by Shaler and Wulff[18] by the following argument. In a mass of powder particles, imaginary continuous lines may be drawn, passing through the centers of the particles and through the centers of the metallic "bridges" where they make contact with one another. These lines may be drawn in such a way that they never emerge from the surface of the metal into the voids between the particles. The aggregate of these lines forms a skeleton. No process can be imagined whereby this skeleton is changed in shape or size unless there is flow within the particles themselves, or across the solid metallic "bridges." If recrystallization has permitted the lattices of the particles to be continuous through these "bridges," as countless micrographs, including that of Fig 3, have shown to be the fact in sintering, then these bridges are made of metal which is in general no different from the metal in the particles themselves. A change in size or shape of the skeleton—and hence of the compact as a whole—must involve flow in the volume of the metal. No redistribution of metal taking place at the surface of the voids between particles can cause any change in the skeleton, which never touches that surface.

If all the voids are connected by channels to the outside of the compact, of course, metal from the outside layers can proceed *via* the gas-phase or by surface-diffusion towards the interior. But this movement ceases as soon as the voids become isolated from the outside. There is other evidence to show that such a transient process can have little influence on the course of sintering—for instance, markings on the surface of compacts do not disappear during sintering.

On the other hand, surface-diffusion and vapor-phase transport do have a function in sintering, but it is not that of changing the density. An aggregate of powder differs from a solid piece of metal chiefly in that it has a great deal more surface per unit of mass. Hüttig[3] and the author[4] show that metal powder made of micron-size particles has so much surface that its free-energy is of the order of 1000 cal per mol greater than that of solid metal. The mass of powder can reach an intermediate state of lower free-energy if the voids between the particles become spherical. Such a spheroidization of the pores has been observed, as pointed out by Rhines.[1] It can proceed by surface-diffusion or by evaporation and recondensation, for it involves only a redistribution of the metal at the surfaces of the voids. It can also proceed by a flow of the metal particles and bridges. A calculation[4] has shown that, in nearly spherical pores (of radius 100μ) inside a copper compact at 850°C, the flow process is more rapid than the evaporation process and probably also than the surface-diffusion process. At the beginning of sintering, however, when the contact areas between the particles are small and the voids have sharper corners, the reverse may be true.

In brief, then, surface-diffusion and vapor-phase transport have a function in sintering, in that they assist the flow process in leading to a spheroidization of the pores. But these mechanisms cannot effect a change in the density of the compact, a change which requires a flow of the metal within the particles themselves.

The First Phase of Sintering

During the first phase, in the sintering of loose powder masses, the particles preserve to a great extent their original shape, and the voids are interconnected. In the second phase, which may best be studied separately, the pores are disconnected entities, and the compact may be considered a porous, but continuous, medium. Sauerwald[25] has shown that the mechanisms in sintering loosely pressed compacts resemble those found in sintering loose powder, whereas heavily compressed compacts already contain disconnected pores in the green state.

If the pores are all joined together and have passage to the outside, there is evidently no difference in gas pressure between the pores and the atmosphere, so that no force is to be expected

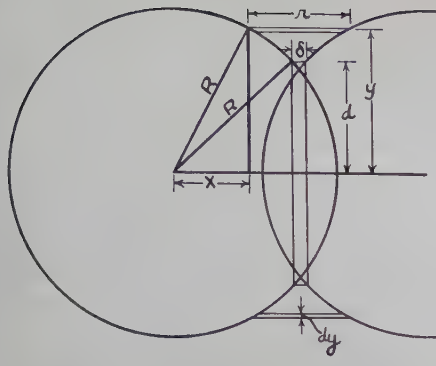


FIG 4—Two spheres, partly coalesced, separated by a minimum distance δ, and subject to attraction across cylindrical elements of length r and of thickness dy.

from this source. The surface tension exists, but it is perhaps more convenient to treat it in this phase as the force of attraction between particles. It has been shown[4,29] that this procedure is justified, since the two forces stem from the same origin.

The force of attraction has been calculated[4] on the following basis: according to the Sommerfeld[11] model of a metal, it is made up of positive ions of infinitesimal size, regularly distributed at the intersections of a geometric lattice; around the ions there is a cloud of fast-moving electrons. The electron density varies, but it is assumed to be uniform as a first approximation. The surface of the metal may be defined as the last layer of ions. The electron cloud does not stop abruptly, however, although its density falls off rapidly outside this layer. The presence of another surface nearby causes the density of the cloud to increase considerably, beyond the surface, and to fall off more gradually. If the surfaces come to within several interatomic distances of one another, there is an appreciable number of electrons moving about throughout the space between them. Each of these electrons is attracted to both the opposing surfaces, so that in effect the two surfaces are attracted to one another because they are both attracted to the electrons between them. The calculation of this force of attraction has yielded, as a first approximation, the following results: two copper surfaces, 30 Å apart, attract each other with a force of approximately 120,000 psi; this force drops to about 55,000 psi if the separation increases to 60 Å, and to about 30,000 psi when the distance is 120 Å. A rise in the temperature from 20 to 700°C decreases these values by only about 15 pct. Cleanliness of the surface is not a serious factor unless thick layers of compounds are formed. The electronic work-function of copper, which depends on cleanliness, can vary from 1 to 5 electron volts without changing the force of attraction more than 10 pct. The calculation cannot be extrapolated to distances less than about 15 Å, because when the surfaces come that close together, the ions begin to repel one another, and the attraction falls off again. The expression is also not valid at great distances, where the presence of foreign ions and atoms interferes with electron movement. An approximate expression can be made to fit the data given above, and the unwieldly equations from which they were calculated are not necessary for practical use. If the distance r separating the surfaces, or elements of surface, is given in inches, then the force in pounds per square inch between them is given, within 10 to 15 pct, by the formula

$$f(r) = 1.4 \times 10^{-2} \frac{1}{r}$$

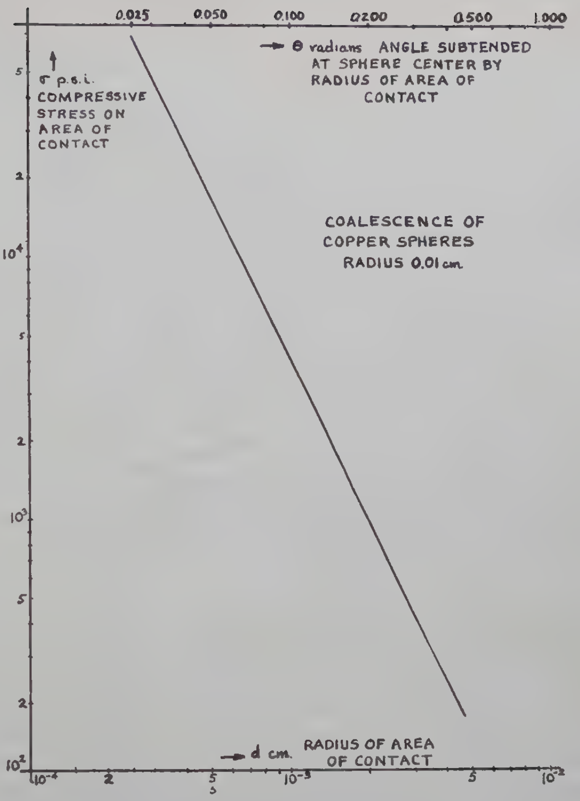


FIG 5—Plot of the compressive stress on the contact area, and of the angle subtended by the radius of that area at the sphere centers, for various degrees of coalescence of copper spheres of radius 0.01 cm.

With this as a quantitative basis, the force of attraction between two coalescing spherical particles may be calculated. Fig 4 shows such a system. The distance δ between them is a region where, as a first approximation, the metal may be considered solid: in this disc-like region the force of attraction becomes balanced by the ionic force of repulsion. Outside this disc, the surfaces gradually fall away from one another, and are under the influence of the force of attraction. The force pulling together the ends of the cylindrical element of thickness dy and height r at a radius y from the centerline is then

$$2\pi y\, f(r)\, dy$$

Integrating from $y = d$ to $y = R$, and remembering that δ is much smaller than R, an expression is found for the total force acting in such a way as to pull the spheres together and compress the disc between them. This expression is

$$F = 4.4 \times 10^{-2} \sqrt{R^2 - d^2} \; ln \left(\frac{2}{\delta} \sqrt{R^2 - d^2} \right)$$

Since the area of the disc is πd^2, the compressive stress acting on it is $\sigma = F/\pi d^2$. The spheres are assumed to remain spherical and to preserve their radius, a good approximation for small values of d. Fig 5 shows the values of this stress as a function of the radius d of the disc, that is, of the degree of coalescence of the two spheres, for copper spheres 0.01 cm in radius (200μ in diam). At first contact, when d is

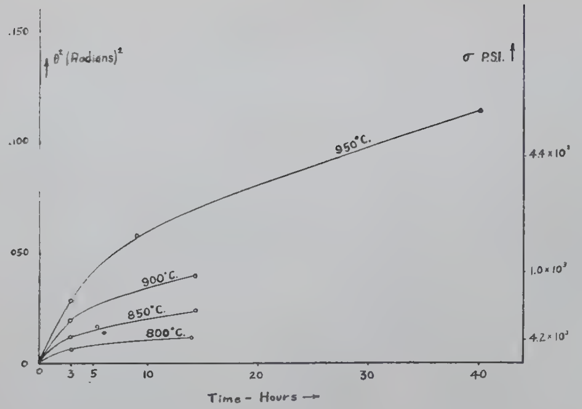


FIG 6—The growth of the area of contact of copper spheres, 0.01 cm in radius, with time at various temperatures. The ordinate is the square of the angle subtended at the sphere centers by the radius of the constant circle. Stresses corresponding to these angles, from the previous figure, are shown at the right.

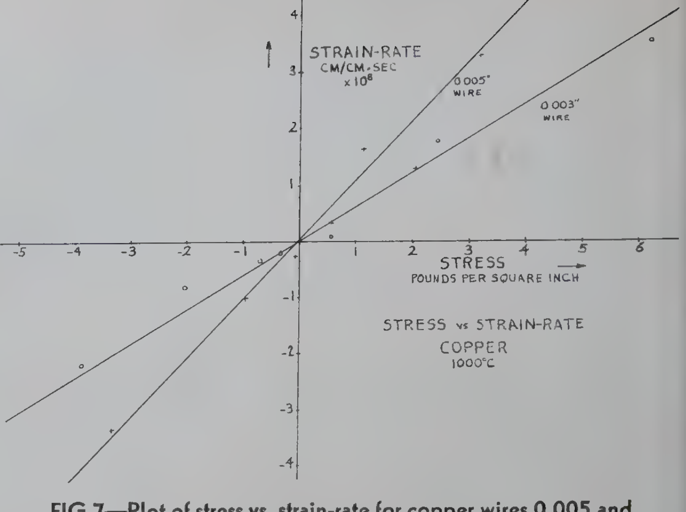


FIG 7—Plot of stress vs. strain-rate for copper wires 0.005 and 0.003 in. diam at various temperatures.
Data from Udin, Shaler and Wulff.

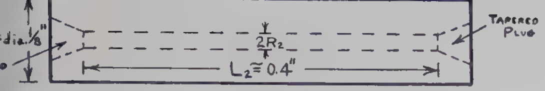
small, the stress of compression on the contact area is very large, and unless there is interference from oxide films or layers an immediate cold-welding occurs, as it does in the friction experiments[7] mentioned earlier, and in those of Bradley on some nonmetallic spheres.[12] Plastic deformation under this stress leads to an increase in the area of contact, and the compressive stress on that area falls off until it becomes less than the least stress necessary to cause plastic flow. But at elevated temperatures, which do not appreciably decrease the force involved, the metal is still able to creep conventionally at these lower stresses. The time factor now enters into the picture, as it does in creep. Soon the compressive stress has fallen to a value lower than the stress-limit for creep, and the first stage of sintering is at an end. By this time, the pores are disconnected, and a new type of flow becomes predominant.

Experiments on the coalescence of spheres have been carried out by the author with the assistance of H. Bernhardt. Copper spheres were selected from a commercial grade of atomized powder (described below) by first sieving for the −70 +100 mesh fraction, then sorting out the particles by rolling them down a narrow ground-glass plate 4 ft long, and inclined at about 4°. The few particles that rolled down the whole length of the plate were selected for the experiments. These particles were packed in carbon-black and heated for 5 hr at 750°C in an atmosphere of dry deoxidized hydrogen at 0.5 mm pressure. After slowly cooling them to room-temperature, the spheres were separated from the carbon-black in an air-classifier. Several particles were then placed in contact with each other in a deep groove in a graphite block. After heating for various periods of time at various temperatures in an atmosphere of dry deoxidized hydrogen, the strings of spheres were observed in a microscope equipped with a micrometer eyepiece. The diameters of the areas of contact and the distances between the centers of the spheres were measured. The angles θ subtended at the center of the spheres by half the radii of the contact areas were plotted against the time at various temperatures. There was some scatter due to the fact that many of the particles were not sound throughout, and that their surfaces, after deoxidation, were not perfectly spherical. The mean deviations from the mean values of θ were of the order of 10 pct. Each point in Fig 6 is the mean of from 5 to 24 spheres, plotted on coordinates of θ^2 and time t. According to Frenkel's analysis,[26] if the coalescence of spheres takes place by a purely viscous flow, the points on such a plot should lie on a straight line passing through the origin, since θ^2 is then directly proportional to the time $\left(\theta^2 = \frac{3}{2}\frac{\gamma}{\eta}\frac{t}{r},\right.$ where r is the sphere radius, γ is the surface tension, and η is the viscosity coefficient). In these experiments the curves are straight only at larger values of the time, and no straight line, however fitted to the points, passes through the origin. Rather, the slope of the line initially decreases rapidly with time at heat, showing that the coalescence starts with a rapid mode of flow (first stage of sintering by creep or even normal slip) and gradually becomes slower until a viscous flow becomes dominant (the line straightens out). Experiments[2] reported recently by Jordan and Duwez agree with this view. Others[5] may not.

In Fig 6, the stresses corresponding to the various values of θ^2 are given on the right-hand scale. These have been taken from Fig 5 ($\sin\theta = d/R$). Note that the linear portion of the curves, representing the second stage of flow, begins at approximately 5000 psi at 800°C, but that non-linearily continues at 950°C until the stress has fallen as low as a few hundred pounds per square inch. Flow in the first stage is thus a process which appears to begin at a critical stress-limit, decreasing as the temperature rises, as in conventional creep. The type of flow required in second-stage sintering cannot have a critical stress-limit, for flow must occur under infinitesimal stress, at a correspondingly small rate, in order to account for experimental results.

Until more is known about the creep of copper at high temperatures under stresses of the order of hundreds of pounds per square inch, it is not possible to predict the rate of this first stage of sintering, when the particles coalesce and the voids between them become disconnected. In highly compressed compacts and in the later stages of sintering of loose or lightly compressed powders, the first stage is by-passed or ended, and the mechanism of sintering involves the slower, viscous, flow described below.

The first stage of sintering is further complicated by all the transient effects described in previous sections, some of which may tend to expand the compacts, some others to shrink it.



G 8—Artificial pore in a short length of copper wire.

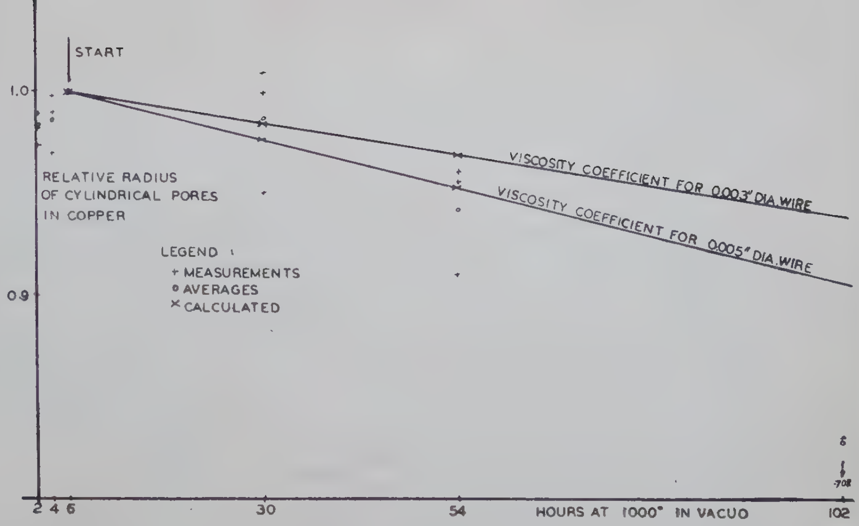


FIG 9—The relative change in radius of cylindrical "pores" in copper, compared with curve calculated from viscosities of copper wires.

Flow in the Second Phase of Sintering

In the second stage, the pores are in general disconnected, and any change in density of the compact involves a change in pore-volume and therefore in the pressure of the gas trapped within the pores. The force of shrinkage, previously manifested as the attraction between surfaces, can now be more conveniently considered as the surface tension.

Surface tensions and pressures of gas such as are encountered in powder metallurgy can form high stresses at the surface of very small pores—stresses great enough to induce plastic flow by the well-known modes of slip, twinning or creep. But it was shown that there can be no density-changes in compacts unless flow takes place inside the particles away from the surface of the pores. Here the effects of the surface tension and of the gas pressure are diluted because they act over a larger area. In the compacts described below, in which marked densification takes place, the pores have an approximate radius of 100 microns. At a distance of only 10 microns away from the surface, the stress induced by the surface tension is less than 3 psi. In the hollow tubes, whose densification is also described below, the radius of the hole is of the order of 2500 microns (0.01 in.), and the stress, even at the surface, is less than 1 psi.

The mechanism of flow at these low stresses has not been extensively investigated. Chalmers[23] has observed the flow of tin at small stresses, and found a viscous flow at room temperature. Udin, Shaler, and Wulff[13] measured the rate of flow of copper at elevated temperatures, under stresses of up to 6 psi on wires 0.005 and 0.003 in. in diam. Fig 7 reproduces their data in terms of stress and strain-rate. These results are consistent with a viscosity, independent of stress, expressed by the relations

$$\eta = 5.94e\frac{66490 \pm 1000}{RT}$$

for 5 mil wire, and

$$\eta = 1.32 \times 10^3 e\frac{53756 \pm 1000}{RT}$$

for 3 mil wire. Kanter[27] and Frenkel[26] predict on theoretical grounds that the phenomenon of self-diffusion should lead to a viscous flow whose heat of activation is the same as that for self-diffusion (57,000–61,000 cal per mol for copper). The viscosities given above have a heat of activation near that range (66,000 and 54,000 cal per mol). Kê[24] has observed a room-temperature grain-boundary flow having the heat of activation for self-diffusion, in both iron and alpha brass. Little can be said with certainty about flow at these stresses save that it is of a viscous nature. Newtonian viscous flow is characterized by the fact that the stress vs. strain-rate curve is linear and passes through the origin. The flow is further complicated by the fact that there is evidently a dependence of viscosity on size. Possibly the self-diffusion coefficient also varies with size.

To show whether a viscous flow of this nature could be responsible for the shrinking of closed pores in sintering, a direct measurement was made. Since the artificial creation of a spherical hole of very small size in a piece of metal entails mechanical difficulties, a cylindrical hole was used. Such holes were drilled (diameters *ca.* 0.02 mm) lengthwise in three short lengths of copper wire. The drilled tubes were then heated overnight at 1000°C in dry deoxidized hydrogen at 0.5 mm pressure, and furnace-cooled. The outside diameter of the tubes was ⅛ in., and their length ½ in. The ends of the holes were tapered to a depth of $\frac{3}{64}$ in., and tapered plugs were made to fit. One end of each was firmly closed by pressing-in the plugs. In the other ends, the plugs were left loose, so that, during heating in vacuo, the holes would be evacuated before becoming sealed. A sketch of such a tube is shown in Fig 8. Being closed, as shown in a previous section, it cannot shrink by surface-diffusion or by evaporation, although by these processes the radius of the hole may expand at the expense of the length (spheroidization), but the radius and length of the hole may both decrease by flow under the action of surface tension. To heat the tubes, they were placed vertically into wells drilled in a graphite block, loosely-plugged ends uppermost. An undrilled ½ in. length of the same wire, similarly annealed and mounted, was used as a control. The heating chamber in which heating was carried out was a long quartz tube, sealed at one end, and fitted at the other with a waxed-in rubber stopper. Two glass tubes, fitted into the stopper, led respectively to a mechanical vacuum pump and gauge and to a source of hydrogen. The quartz tube could be evacuated and then inserted into a chromel-wound furnace. In this way, high-temperature seals were avoided, and heating and cooling-times would be cut to a minimum. The same furnace technique was used in the experiments on the coalescence of spheres and on the sintering of compacts, described elsewhere in this paper. The source of hydrogen was a commercial cylinder, from which the pressure was reduced by a conventional reducing valve to about 15 psi. The gas went to a purification train consisting of four tubes containing respectively heated copper gauze, indicating Drierite, palladium-alundum, and activated alumina. From this train, the hydrogen passed through a constriction-flowmeter, and then through a 4 ft length of 1.2 mm capillary tubing before entering the quartz furnace-chamber. The capillary furnished a pressure differential such that atmospheric pressure could be maintained in the reducing train and flowmeter, whereas a vacuum of 0.5 mm could be easily obtained in the furnace-chamber.

The small copper tubes were first subjected to a series of three 2-hr heats at 930°C, and thereafter, since density measurements showed the metal had nearly reached stability under these conditions, to a series of 24-hr heats at 1000°C. After each heat the tubes were radiographed; their external dimensions were measured with a micrometer caliper, and their density was determined to four significant figures pycnometrically. The dimensions of the holes were found from the density determinations, and were checked by measuring the radiographs on a film-reader.

The function of the hydrogen leak at 0.5 mm pressure was to insure the reduction of any oxygen leakage and also to reduce all oxide in the metal, without introducing into the "pore" enough gas to provide appreciable pressure until the shrinkage had become considerable. Fig 9 shows the relative radius of the cylindrical "pores" plotted against time-at-heat. Also plotted are the slopes of the calculated curves to be expected if the mechanism of flow is the same as that found in wires by Udin, Shaler, and Wulff.[13] These two curves are plotted for the viscosities observed on 0.005 and 0.003 in. wires at 1000°C. It is expected that the size-effect on the value of viscosity should disappear rapidly at larger sizes. In the tubes, the wall thickness is about 0.050 in., so that the slope should be somewhat greater than that given for 0.005 in. wires. The calculation of these curves was done as follows (see Fig 9): The incompressibility of the metal requires that the same weight enter into and flow out of a cylindrical shell of thickness dA at radius A from the pore centerline. The outermost and innermost shells yield the equations

$$\frac{dA}{dt} = \frac{R_2}{A}\frac{dR_2}{dt} = \frac{R_1}{A}\frac{dR_1}{dt}$$

The strain-rate at any radius A, in terms of the rate of decrease of R_2, is

$$\frac{d\epsilon}{dt} = \frac{d}{dA}\left(\frac{dA}{dt}\right) = -\frac{1}{A^2}R_2\frac{dR_2}{dt}$$

Since the stress-strain relation for viscous flow is

$$\sigma = \eta\frac{d\epsilon}{dt}$$

the heat dissipated by flow per unit volume per unit time, at radius A, is then, after Frenkel[26]

$$dE_F = 2\sigma\epsilon = 2\eta\epsilon\frac{d\epsilon}{dt}$$
$$= 2\eta\left(\frac{d}{dA}\left(\frac{dA}{dt}\right)\right)^2$$

In a length l of the tube

$$E_F = 2\eta\int_{R_2}^{R_1}\left(\frac{d}{dA}\left(\frac{dA}{dt}\right)\right)^2 2\pi A l dA$$
$$= 2\pi\eta l R_2{}^2\left(\frac{dR_2}{dt}\right)^2\left(\frac{1}{R_2{}^2} - \frac{1}{R_1{}^2}\right)$$

The loss in surface energy per unit time, due to the reduction of both inside and outside surfaces, is, if γ is the surface tension,

$$E_s = -\frac{d}{dt}(2\pi l\gamma(R_2 + R_1))$$
$$= -2\pi l\gamma\left(1 + \frac{R_2}{R_1}\right)\frac{dR_2}{dt}$$

Equating E_F to E_s, and simplifying,

$$\left(1 - \frac{R_2}{R_1}\right)dR_2 = -\frac{\gamma}{\eta}dt$$

Using the incompressibility condition, and integrating from the initial radii R_{10} and R_{20}, there results

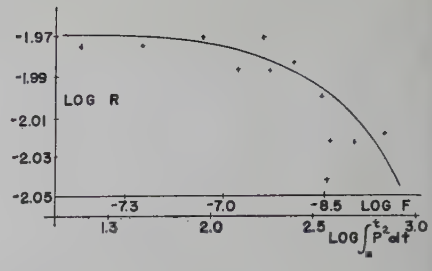
$$(R_{20} - R_2) - (R_{10} - R_1) = \frac{\gamma}{\eta}t^*$$

from which the curves of Fig 9 are drawn, using the values of γ and η at 1000° from Udin, Shaler and Wulff.[13]

It is clear from these curves that the hollow cylinders do shrink under the influence of surface tension and it is probable that the size effect is real, and must be taken into account in sintering theory; the particle-size as well as the pore-size is a variable affecting the sintering rate of a compact.

Rate of Sintering in Second Stage

The same calculation as that made for a cylindrical pore has been made for a spherical pore by Frenkel.[26] In a vacuum, according to him, the energy dissipated in viscous flow becomes, if R is the pore radius at any time,



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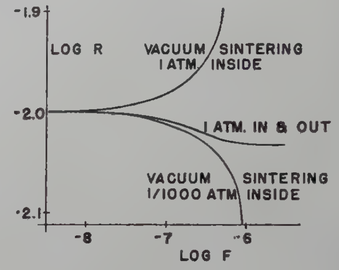

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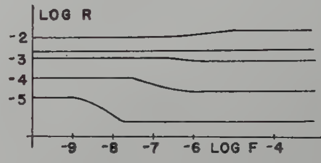

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FIG 10—Change in average pore-radius during sintering of unpressed copper powder at 850°C.

After Shaler and Wulff.*

FIG 11—The change of radius of pores during various conditions of sintering in noble gas.

The top and bottom curves eventually level out also. After Shaler and Wulff.

FIG 12—The changes in the radii of pores of various initial radii, under conditions of vacuum sintering of compacts in which noble gas is trapped at an initial pressure of one atmosphere.

After Shaler and Wulff.

$$E_F = \frac{32\pi\eta R}{3\rho}\left(\frac{dR}{dt}\right)^2$$

where ρ is now the density of the porous metal surrounding the spherical void. Since the compact is usually very large compared to the void, its external radius is neglected. The density ρ varies with time during shrinkage of the compact, and therefore the rate of sintering must be measured by a parameter which combines both the time and the changing density. One such parameter, which greatly simplifies the calculations, is

$$F = \frac{3}{8\eta}\int_0^t \rho^2\,dt$$

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* The right-hand member should be $\frac{1}{2}\frac{\gamma}{\eta}t$ (see Discussion by Eshelby) and Fig 9 has been redrawn with the correct value.

* Fig 10, 11 and 12 are reproduced from Fig 2, 3 and 4 of "Mechanism of Sintering" by A. J. Shaler and John Wulff. *Ind. and Eng. Chemistry*, May 1948. Reprinting is by permission of the copyright owner, the American Chemical Society.

Here the density ρ is introduced as a fraction of the density of solid metal. Equating E_F to the loss in surface energy E_s, as before, leads in the case of a spherical pore to

$$F = \frac{R_0}{2\gamma} - \frac{R}{2\gamma}$$

where R_0 is the initial pore radius.

Unpressed masses of powder particles, closely sized by sieving, were heated in vacuo at 850°C. The initial radius of the pores, R_0, was calculated by assuming that the number of pores was equal to the number of particles. This assumption is valid in the case of a regular geometrical packing of the particles. Since the density of the loose mass was 0.51 of that of copper, and a simple cubic array would have a density of 0.52, this condition was judged to be fairly well obeyed. The effective radius of the pores was consequently found from the volume of voids divided by the number of particles. Since the average radius of the particles was 0.011 cm, that of the pores was 0.0108 cm. The validity of assuming that the voids are spherical is discussed in detail by Shaler[4] and by Shaler and Wulff,[18] and found to be satisfactory for voids which are not needlelike or flake-like. From Fig 6 it is observed that the end of the first phase of sintering is reached at 850°C when the contact-area radius is less than $\frac{1}{10}$ the radius of the particle. The densification corresponding to this point is very slight, so that in studying the progress of sintering of such copper compacts at this temperature, the first phase may be neglected. At higher temperatures it would have to be taken into account. After heating these compacts for various periods of time, their densities were measured, and the time and density values were combined to give values of the parameter F. When these were plotted on logarithmic paper against the changing radii of the pores, also found from the density, the points of Fig 10 resulted. The calculated curve in the figure corresponds to a coefficient of viscosity with a heat of activation near 66,000 cal per mol.[4,18] The viscosities obtained in Udin, Shaler and Wulff[13] have heats of activation of 66,490 cal per mol for 0.005 in. wire, and 53,756 cal per mol for 0.003 in. wire. The diameter of the particles used in the compacts was 0.008 in.

So far no account has been taken of the pressure of gas trapped within the pores. Three kinds of gas may be present: those which dissolve in the metal or form a compound with it; those which diffuse through the metal at an appreciable rate; and those which neither diffuse, dissolve, nor react. The first kind have a pressure P_e dictated only by the temperature; when the pore shrinks, the gas is not compressed, but instead more of it goes into solution or reacts; the pressure does not change, and is constantly opposed to the stress introduced by the surface tension. Accordingly, if there is a pressure P_0 outside the compact, the pore shrinkage obeys the expression

$$\frac{dR}{dt} = \frac{3}{8\eta}\left[(P_0 - P_e)R - 2\gamma\right]\rho^2$$

Solving for F leads to[4]

$$F = \frac{2.3}{P_0}\log\frac{(P_0 - P_e)R - 2\gamma}{(P_0 - P_e)R_0 - 2\gamma}$$

If P_e is larger than P_0, it is observed that pores initially of large size do not shrink, but expand on heating; that is, the compact swells. In copper, where γ is of the order of 1400 dynes per cm, pores larger than 5×10^{-3} cm in radius swell if $P_e - P_0$ is one atmosphere.

Gases of the second kind are more troublesome. The pressure of such gases depends on two factors: how fast the pore is shrinking; and how far inside the compact the pore is situated. No simple expression for the rate of sintering can be found except for particular cases. For instance, in the case of a very rapidly diffusing gas, the pressure stays generally low and may be neglected.

The third kind, the noble gases, are of more general interest, because all compacts pressed in air contain oxygen and nitrogen. The oxygen is generally removed during the first stage of sintering, either by the reducing atmosphere of the furnace, or in the form of compounds having a low equilibrium pressure. The nitrogen remaining behind is noble to many engineering metals. The expression for the parameter F is, in the case of a noble gas,

$$F = \int_{R_0}^{R}\frac{dR}{\frac{P_0R_0^3}{R^2} - 2\gamma - P_0'R}$$

The labor of solving this equation is great, and it has been performed[4] for one particular case only; namely, for pores 0.01 cm in radius, containing a noble gas initially at one atmosphere, the compact being sintered in a noble gas also at one atmosphere. Fig 11 compares the progress of sintering under these conditions with the progress in the case of vacuum sintering of compacts with and without any trapped gas. The limiting case where $P_0' = 0$ is easier to treat and yields:

$$F = -\sqrt{P_0R_0^3}\left[\frac{1}{2\gamma x} + \frac{1}{2\gamma}\left(\frac{1}{2\sqrt{2\gamma}}\,ln\,\frac{x - \sqrt{2\gamma}}{x + \sqrt{2\gamma}}\right)\right]_{\sqrt{P_0R_0}}^{x\sqrt{\frac{1}{R}}}.$$

where $$x^2 = \frac{P_0R_0^3}{R^2}$$

The curves corresponding to this expression, for P_0 equal to one atmosphere, are given in Fig 12. Pores larger than a critical size (2.4×10^{-3} cm radius) are seen to expand; finer pores shrink.

Fig 11 and 12 show another phenomenon: the change in pore-size takes place most rapidly during a relatively short time-range. The time range depends only on the pore-size, not on the conditions of gas pressure. Thus in Fig 11, the change, whether of expansion or shrinkage, is most rapid in the range of log F from -6 to -7 for pore-radii of 0.01 cm. From Fig 12 it is evident that the finer the pores are, the sooner they change. A compact pressed in air containing an assortment of pores ranging in radius from 0.0001 cm to 0.01 cm, would, upon sintering in vacuo at 850°C, first begin to shrink, in a very few minutes; and later, after an hour or more, it would expand again, and finally reach a stable density. Such a sequence is clearly shown in the work of Drapeau in cylindrical copper compacts.[28]

In heavily pressed compacts of ductile metal powders, the voids, originally isometric, are compressed to a flake-like shape. The radius of curvature in the direction of pressing is then much larger than it is in a direction perpendicular to the pressing direction. Although the gas pressure is hydrostatic, the surface-tension force is not, and the pores may at first shrink in the lateral direction, while axially they are effectively larger and do not yet change. At a later time they may expand in the direction of pressing while remaining unchanged laterally. The final length of a cylindrical compact so compressed would be unchanged after a short sintering period, but the radius would have decreased. After a longer time of sintering the length might be greater, the diameter having suffered no further change. In such a case a short sintering time would yield a denser product than a long sintering time, and the shrinkage of at least one dimension could be held to a minimum.

The porosity of a compact is not a direct measure of its fracture strength, as Sauerwald has often pointed out.[25] The shape of the voids is an important factor, because spherical pores are not as effective in concentrating stresses as are shapes containing sharper curvatures. Furthermore, long times of sintering favor conventional grain-growth, which may have a deleterious effect on strength. A more exact knowledge of the changes in shape and dimensions of pores and grains could be acquired by further study along the lines described here, and might permit powder metallurgists to select, on a more scientific basis, the proper pressures, temperatures, and times necessary to treat a compact to its best possible physical properties.

Conclusions

There remain many unsolved problems. For instance, it would be useful to know the atomistic nature of the viscous flow observed to take place at high temperatures under low stresses. In particular, the size effect observed by Udin, Shaler and Wulff[13] and its relation to particle-size require more study. The role of oxide-films, of the thickness commonly found on metal powders, needs quantitative treatment. Such films undoubtedly affect the surface tension, the force of attraction, and govern in a large measure the pressure of gases trapped within the pores. In view of the extensive use of hydrogen-containing sintering atmospheres, the kinetics of sintering in the presence of diffusible gases is a field in which more work must be done. Finally, a great deal more experimental work must be done to test the hypotheses brought out in this paper regarding the force of attraction and the flow of metals under small stresses.

The sintering process is an extremely complicated one. In addition to the changes known to occur during the heat-treatment of massive metals—recrystallization, grain-growth, and others—the presence of a large surface-to-volume ratio increases the effects of transient phenomena such as the reactions and desorptions that occur at the surfaces of metals.

This study has given a more quantitative evaluation than any heretofore carried out of some of the mechanisms that are in operation during sintering. Among these are the force of attraction between metal particles, the role played in the first stage of sintering by plastic flow or creep, and the nature of the last stage of the process, in which a viscous flow takes place under the combined action of surface tension and gas pressure.

Considerable attention has also been given to the part played in sintering by the transport of metal through the mechanisms of recrystallization, flow, surface-diffusion, and evaporation.

It has been shown that copper, and by inference, other metals, possess in the solid state a surface tension not widely different from that of the molten metal, and that this force alone is capable of bringing about changes in density in powder compacts. The question of why some compacts shrink, others swell, and still others do both simultaneously in different directions and at different times has been discussed. Methods of calculation have been outlined wherewith a powder metallurgist can evaluate the best conditions of time, temperature, particle-size and pressure required to meet his specifications.

In a limited range of cases it is now feasible to predict the course of sintering with some precision, and some observations, which until now have been puzzling to students in this field, can now be interpreted with less difficulty.

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Discussion

(F. V. Lenel presiding)

H. H. HAUSNER*—I am surprised that Shaler in his excellent study on sintering does not apply electrical test methods in order to determine and distinguish the various stages of sintering. Electrical resistance or conductance measurements on sintered compacts permit a deeper insight in the process of sintering and especially in the earlier stages—or as Shaler calls it in the first phase of sintering, than any other methods.

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The electrical resistance of a sintered material is composed of two different types of resistances: the particle resistances and the resistances between the particles which we call contact resistances.* In a general way (and before recrystallization) the total of the particle resistances will be the same whatever the particle size is, or whatever the respective degree of sintering of the compacts is. The contact resistances between the particles however will greatly change with the bond between the particles and will therefore be an indicator for the respective stages of sintering.

It is not only the electrical resistivity which permits conclusions on the bond between particles but also the temperature coefficient of resistance. Oxide layers, impurities or other material on the grain boundaries will greatly affect the contact resistance and especially influence its change with the temperature.

The results of a comprehensive study on the electrical properties of sintered material, especially describing the effect of the degree of sintering on the electrical resistivity of compacts will be published in the near future.

A. J. SHALER (author's reply)—I should like to thank Dr. Hausner for his excellent suggestion. I look forward with interest to the publication of his results. Owing to the complexity of the sintering process and the number of variables changing simultaneously during heating, I prefer, whenever possible, to simplify the problem by studying such models as a string of small perfect particles, or a synthetic pore. If, at some time in the future, I understand fully what is going on in these simple models, then I shall feel free to carry out experiments on the enormously more complicated problems existing in compacts made of irregular particles of various sizes and of different compositions. The state of the science concerning contact resistance and the passage of the electric current through complex surfaces in contact with one another is not yet such as to permit me to use it with much confidence as a research tool.

E. F. SWAZY† and L. S. BUSCH†—Generally, the powder metallurgist is concerned with the space between metal powder particles more than the particles themselves. In making structural parts, he is concerned with minimizing pore space or eliminating it. In making bearings, filters, or any parts in which the pores are later filled, he is concerned with the shape, size, and degree of continuity or discontinuity of these spaces between the powder particles. Any work deserves great praise which sheds light upon the behavior of these spaces during the treatments usually afforded articles made from metal powders. Dr. Shaler's paper describes such work.

In the treatment of fine copper powder to reduce the oxides formed during storage, appreciable sintering occurs even at very low reduction temperatures. If the cake so formed is broken up, then changes which have occurred during the reduction (which can be considered a step in the elimination of the so-called transient phenomena) will affect the subsequent states through which a compact goes during sintering. We feel that any attempt to divorce completely the "steady state" and "transient phenomena" is a dangerous one and might lead to oversimplification of a difficult problem. One can consider these phenomena separately but cannot separate them finally.

We believe that the question of change in pore discontinuity during sintering deserves some discussion. It seems very dubious to us that the pores, resulting from the pressing of a compact from any metal powder particle which is not flat, ever become discontinuous.

Consider a three dimensional figure similar to Fig 4; that is, a closely packed group of spheres. It is difficult to imagine a complete discontinuity of the pores until the compact becomes completely dense, particularly if the particles retain some measure of their spherical shape on all surfaces forming a pore wall.

If the particle shape is changed before complete densification, as by repressing, it is conceivable that the pores might become discontinuous. But, as shown by the table that follows, porosity is still continuous even after severe repressing. It is conceivable then, that surface diffusion and evaporation can be considered part of the steady state phenomena. Certainly the rate at which both of these proceed would increase rapidly with increasing temperature and would also increase with time at a high temperature.

In the following table is shown the relative degree of porosity of copper compacts made from a minus 100 sieve, hydrogen reduced, copper powder sintered at 900°C for one-half hour and repressed at various pressures. The pressed density was 7.5 g per cc and the sintered density was approximately 85.5 pct of absolute in each case.

The degree of permeability was measured by noting the time required for a pressure of 90 lb of air on one side of the compact to fall to atmospheric pressure on the other. The figures indicate that the pressure fell 6.6 times as fast in the 89 pct dense specimen as in the 94.4 pct dense one, but the important point is that the pores did not become discontinuous in any case. Neither do the pores in materials which develop a liquid phase become discontinuous. Porosity as low as 0.5 pct can be detected by liquid absorption methods in such materials as carbides or other high density materials and also in some materials which are pressed, sintered, and repressed to densities as high as 96 pct of absolute.

Final Density g per cc	Pct of Absolute Density	Relative Permeability to Air
8.00	89.	5
8.25	92.8	5
8.32	93.5	1
8.40	94.4	¾

A. J. SHALER—Mr. Busch has brought up an interesting question concerning the closing of cavities. I think evidence exists that in pressing, a large proportion of the voids become isolated, and contain trapped gas at a pressure somewhere near the pressure with which the compact has been compressed. Some very thin compacts have even been observed to explode. I see no explanation unless the gas is trapped in sealed-off voids at high pressure. If Mr. Busch has made a three dimensional model of a group of spheres close-packed or otherwise, he cannot have failed to notice that in between them, on certain planes, there is a definite neck through which the passage of a gas or liquid is limited. The area of such necks must decrease in the first stage of sintering when the contact areas between spheres increase. If the sphere centers approach one another the neck is also gradually throttled down. It does not take very much increase in contact area or decrease in the distance between centers to close them completely. In later stages of sintering I cannot see any other explanation for the swelling of compacts than the presence of a force directed outward and acting on the void surface; that force to my mind can only be a gas pressure.

Other evidence in this connection is shown in the experiments reported on Fig 2, in which I was able to heat up compacts of spherical copper particles under isothermal conditions in a gas at a pressure of one atmosphere. The density of the compact increased at a gradually decreasing rate until, after a prolonged period of heating, an equilibrium density was obtained. These compacts were then heated further in vacuo. By thus forming a differential in pressure between the gas inside the voids and the gas outside the compact I was able to bring the density gradually down to a lower equilibrium value.

The reason for the residual permeability in carbides or in copper compacts must be that there is a wide initial variation in the void sizes. That might in turn be due to a wide variation in the particle size or to an irregular distribution of the particles.

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* H. H. Hausner: The Effect of Particle Size on the Electrical Properties of Sintered Materials. Powder Metallurgy Bull. (1948) 3, 4–8.

† P. B. Mallory & Co., Inc.

In that case, regions containing large pores take a considerably longer time to reach the end of the first phase of sintering than those containing only small ones. I think if regular geometrical patterns of equal spherical particles could be put together and sintered you would find the permeability reaching zero after long heating.

F. N. RHINES—If I remember correctly, Mr. Busch's sintering conditions were one hour at 900°. We have made some observations on changes in pore shapes at various temperatures and times. In the specimens that we used, the pores were definitely still connected and far from being spherical in one hour at 900°. However, as time goes on, the pores do spheroidize and by 1000 hr at 900° they are very close to being spherical and quite obviously not connected. I think that the observation under discussion is to be associated with too short a time to get into the condition of the samples to which we refer.

J. D. ESHELBY*—There are slight numerical errors in the formulas given by Dr. Shaler for the rate of closing of both cylindrical and spherical cavities. In view of the importance of these results it may be of interest to show how they may be derived by elementary, if rather tedious, methods.

In the case of the cylindrical cavity it is clear that a square of unit side with a diagonal pointing towards the center of the cavity suffers a pure shear 2 de/dt per unit time. The work required to produce this shear is $\eta(2\,de/dt)^2$, twice Dr. Shaler's value.

In more complex cases this simple argument cannot be applied. We may start from the basic law of viscosity in the form: a unit surface normal to the direction of the velocity gradient has a tangental force acting on it of magnitude $\eta \times$ velocity gradient and directed parallel to the velocity. For any particular problem a volume-element can be chosen all of whose faces are subject only to shear stresses. If we choose a system of reference in which the center of the volume-element is at rest the work done on each face in unit time is then the product of η, the velocity gradient, the area of the face and the velocity of the surface in its own plane.

For the cylindrical case the appropriate volume-element is the cube, one of whose faces is the square ABCD, with BD along a radius. After unit time it has the shape A′B′C′D′. If AB = 1, then AA′ = BB′ $= \frac{1}{2}\sqrt{2}\,de/dt$. AB has undergone a rotation and a displacement Aa = bB′ $= AA/\sqrt{2} = \frac{1}{2}de/dt$ which is its velocity in its own direction. The shear strain is, as before, $2de/dt$: it is the velocity gradient normal to AB. The work done on the face AB per unit time is thus $\eta(de/dt)^2$. There are equal contributions from the other three faces so that the rate of dissipation of energy per unit volume is $4\eta(de/dt)^2$ as before. The corresponding value for the rate of closing of a cylindrical cavity is

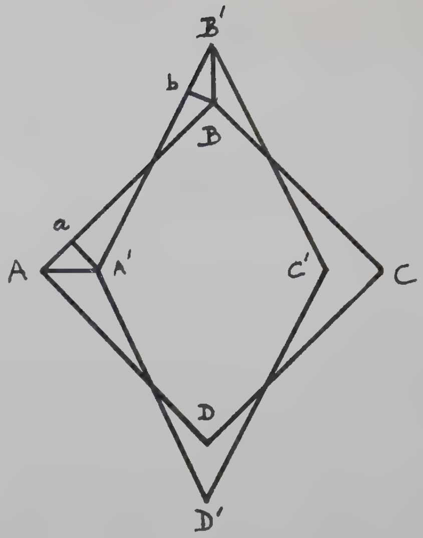

FIG 13—Sketch to illustrate calculation of rate of closing of a cylindrical cavity.

$$dR/dt = -\tfrac{1}{2}\gamma/\eta.$$

For the spherical case the appropriate volume-element is a regular octahedron with the line joining a pair of opposite vertices pointing along the radius (Fig 13). The medium suffers an extensional strain de/dt per unit time in the radial direction. To preserve constancy of volume there must be a contractional strain $\frac{1}{2}de/dt$ in directions at right-angles to the radius. The three diagonals of the octahedron are thus parallel to the principal axes of strain: in such a case it is known* that its faces are subject only to shear stresses. The velocity gradient between opposite faces is easily shown to be $\sqrt{2}(de/dt)$. Suppose that the previous figure now represents a section of the octahedron with B,D as opposite vertices and A,C the mid-points of a pair of opposite edges. If the edge of the tetrahedron is 1 then BD $= \sqrt{2}$, AC = 1. Aa now becomes $(de/dt)/4\sqrt{3}$ and bB′, $(de/dt)/\sqrt{3}$. The component along AB of the velocity of the face of the octahedron varies linearly between these limits on passing from A to B. The mean value over the face is found to be $(de/dt)/2\sqrt{3}$. The area of the face is $\sqrt{3/4}$. This leads to $\sqrt{2}\eta(de/dt)^2/8$ for the work done on this face per unit time. There are eight such faces and the volume of the octahedron is $\sqrt{2/3}$ so that the rate of energy dissipation per unit volume is $3\eta(de/dt)^2$.

For a spherical cavity in an infinite medium $de/dt = -2(dR/dt)R^2/A^3$ so that the total rate of dissipation of energy is

$$E_F = 12R_0^4\eta\left(\frac{dR_0}{dt}\right)\int_{R_0}^{\infty}\frac{4\pi}{A^6}A^2dA$$
$$= 16\pi\eta R_0\left(\frac{dR_0}{dt}\right)^2$$

that is, $\frac{3}{2}$ times the value given by Frenkel. The error in Frenkel's paper* is the following, using his notation: with spherical polar coordinates the non-vanishing components of his v_{ik} are v_{rr}, $v_{\theta\theta}$ and $v_{\varphi\varphi}$, not merely v_{rr}, as he states. The condition of incompressibility gives at once $v_{\theta\theta} = v_{\varphi\varphi} = \frac{1}{2}v_{rr}$. In his integral $v_{rr}{}^2$ must therefore be replaced by $v_{rr}{}^2 + v_{\theta\theta}{}^2 + v_{\varphi\varphi}{}^2 = \frac{3}{2}v_{rr}{}^2$.

The rate of closing of the cavity is

$$dR/dt = -\tfrac{1}{2}\gamma/\eta$$

It is interesting to note that this is the same as for the cylindrical cavity.

These and other results can also be obtained directly from an anology between viscous and elastic problems pointed out by Goodier.† Suppose that an incompressible elastic solid (that is, one with a Poisson's ratio ½) is deformed by the application of surface or body forces, and that the components of elastic displacement at a point are u, v, w. If the shear modulus μ is replaced by a coefficient of viscosity η then u, v, w are the velocities of flow of a viscous liquid under the same forces. The rate of dissipation of energy is found from the elastic energy by replacing μ by η and multiplying by 2, since we require stress × rate of strain instead of the familiar ½ stress × strain.

Thus, for example, the rate of contraction of the spherical cavity is equal to the displacement of the surface of a spherical cavity in a medium with shear modulus η when the same surface-tension forces are applied. The energy need not be introduced, since the solution of the elastic problem is known. As a matter of fact the elastic energy per unit volume is $\frac{1}{2}Ee^2$ where E is Young's modulus ($= 3\mu$ for an incompressible solid) and e is the radial strain. The dissipation in the viscous case is thus $3\eta(de/dt)^2$ as before.

Summary

There is an error in the formula given by Frenkel for the rate of energy-dissipation round a closing spherical pore. This has the effect of replacing the numerical factor $3\frac{2}{3}$ by 16 in Dr. Shaler's expression for E_F. For the corresponding cylindrical problem the rate of dissipation should be $4\eta(de/dt)^2$, not $2\eta(de/dt)^2$.

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* See for example A. Nadai: *Jnl. App. Phys.* (1937), **8**, 205.

* J. Frenkel: *Jnl. of Phys.* USSR (1945), **9**, 385.
† *Phil. Mag.* (1936) (7), 678.

It is shown how these results may be obtained by elementary methods.

A. J. SHALER—I thank Dr. Eshelby for bringing up this point and for his elegant demonstration. He is entirely correct as I discovered some three or four weeks ago when I recalculated this entire problem by yet a third approach, namely the Rayleigh equations of hydrodynamics. The correction, as you see, alters the constant factor in the result. I have recalculated the curves of Fig 9 accordingly, and have also added some experimental points obtained since the time of writing. The results are not precise enough to show any different agreement with the corrected curves, which are shifted by a small amount. Further experiments are in progress.

R. SHUTTLEWORTH*— Goodier[30] has pointed out that the problem of the steady flow of a viscous fluid and the elastic displacement of an incompressible solid are mathematically identical. Suppose that two isotropic homogeneous bodies of the same shape—one purely elastic and incompressible, the other purely viscous—are loaded in the same way; the displacement of the elastic body is given by the product of μ and a function of position, while the velocity in the viscous case is given by the product of η and the same function, where μ and η are the shear modulus and the coefficient of viscosity.

It is useful to apply this correspondence to the calculation of the rate of shrinkage of a viscous fluid that contains a large number of equal spherical pores, of radius R, due to surface tension (Dr. Shaler's model of sintering). The elastic problem is the deformation of the corresponding body formed from an incompressible but shearable material, due to a hydrostatic pressure $-2\sigma/R$ inside all the pores and zero pressure outside the body, where σ is the surface tension. Because the material is incompressible the deformation depends only upon the pressure difference between the inner and outer boundaries (this immediately follows from principles of superimposition of strains and the proportionality of stress to strain); the problem thus reduces to the deformation due to a hydrostatic pressure $+2\sigma/R$ outside the body and zero pressure inside the pores.

The hydrostatic pressure produces shears in the walls separating the pores, which cause a reduction in volume of the pores (the volume of the solid, of course remains constant). It is possible to treat the body as a homogeneous continuum, and every element of volume V (supposed so large that it contains many pores) has a simple dilatation strain dV/V which is independent of the size and shape of the body, and of the position of the element. The displacement between any two points is proportional to their initial separation.

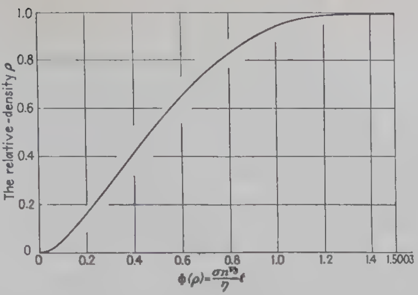

FIG 14—The increase at relative density with time at sintering.

To make the theory quantitative it is necessary to find a relation between the dilatation and the pressure $2\sigma/R$. Here the approximation is made that the decrease in volume of a porous sphere is the same whether the pores are uniformly distributed or are all collected together at the center of the sphere. Love[31] gives an expression for the radial displacement μ of the outer surface of a solid shell with internal and external radii a and b, due to an external pressure, from this expression

$$\frac{dV}{V} = \frac{3u}{b} = -\frac{3}{4\mu}\frac{a^3}{b^3 - a^3}\frac{2\sigma}{R}$$

A more accurate calculation could perhaps be made along the lines indicated by Bruggeman.[32]

The relative-density ρ is defined by, $\rho = V_m/V$ where V_m is the volume of metal in an element of volume V, therefore

$$\frac{dV}{V} = -\frac{d\rho}{\rho};\ \frac{a^3}{b^3 - a^3} = \frac{1-\rho}{\rho}.$$

If there are n pores per unit volume of *metal*, then

$$\frac{1}{R^3} = \frac{4\pi}{3}\frac{\rho}{1-\rho}n$$

n can be calculated from the initial density and the initial pore radius; it does not change with time. And so

$$d\rho = \frac{3}{2}\left(\frac{4\pi}{3}\right)^{1/3}\frac{\sigma n^{1/3}}{\mu}\rho^{1/3}(1-\rho)^{2/3}.$$

In the viscous case each element of volume (together with its pores) flows towards the center of the spherical specimen with a velocity which is proportional to its distance from the center. The rate of decrease $-dV/dt$ of an element of volume V, corresponds to the decrease of volume $-dV$ in the elastic case:

$$\frac{d\rho}{dt} = \frac{3}{2}\left(\frac{4\pi}{3}\right)^{1/3}\frac{\sigma n^{1/3}}{\eta}\rho^{1/3}(1-\rho)^{2/3}.$$

The density increases uniformly throughout the whole body, at a rate which is independent of the size and shape of the body. When the last equation is integrated the relative-density is obtained as a function of time t,

$$\frac{\sigma n^{1/3}}{\eta}t = \frac{2}{3}\left(\frac{3}{4\pi}\right)^{1/3}\int_{\rho_0}^{\rho}\frac{d\rho}{\rho^{1/3}(1-\rho)^{2/3}}$$
$$= \Phi(\rho) - \Phi(\rho_0)$$

where ρ_0 is the relative-density at time $t = 0$. I am grateful to my colleague Mr. J. K. Mackenzie for evaluating the integral $\Phi(\rho)$, which is plotted in Fig 14. With the substitution $x = (1-\rho)^{1/3}/\rho^{2/3}$, the integral can be expressed in terms of known functions. If Dr. Shaler's model is correct this equation enables the ratio σ/η to be found from the variation of the density of a powder compact with time.

Dr. Shaler, in his treatment of this problem, ignored the fact that all the pores in the body are closing simultaneously; and found that the velocity of flow decreased with the distance from a pore. This is not correct. An observer situated at the center of a pore and moving with the pore, who smooths out the change in direction of flow around the other pores, will observe that, at distances larger than the separation at pores, the velocity of flow increases in proportion to the distance.

Summary

Dr. Shaler's treatment of the rate of increase of density of a porous body is not valid, because he does not take account of the simultaneous closing of all the pores. A treatment based on the solution of the corresponding elastic problem shows that the relative-density ρ increases with time t according to the equation,

$$\frac{\sigma n^{1/3}}{\eta}t = \Phi(\rho) - \Phi(\rho_0).$$

where n is the number of pores per unit volume of *metal* (that is, it does not change with time) and the function $\Phi(\rho)$ is shown in Fig 14.

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31. A. E. H. Love: Elasticity. Dover: New York (1944) 142.
32. D. A. G. Bruggeman: *Annal. der Phys.* (1937) **29**, 160.

A. J. SHALER (author's reply)—I thank Dr. Shuttleworth and his colleague, Mr. Mackenzie, for the excellent discussion and for providing us with an explicit solution to the function F which I have left unintegrated. The possible skin effect, or size effect, described in the Udin, Shaler and Wulff paper[13] may make it necessary to alter both Dr. Shuttleworth's model and my own. In the case of Dr. Shuttleworth's model, the change would lead to a more serious drawback, for it would be necessary to evaluate in a new light the validity of the approximation of a porous compact by a solid body with a single cavity at the center, and also the validity of extending his solution to other than spherical compacts, two unnecessary evaluations in the case of my analysis, in which the relative density is introduced into the graphical integration of F as an experimental value. A second drawback to the use of Dr. Shuttleworth's explicit solution is that the value of ρ_0 at the end of the first stage of sintering is not known, so that the value of the constant $\Phi(\rho_0)$ must in any case be deduced from experimental results.

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Dr. Shuttleworth's criticism concerning the velocity of flow decreasing with distance from a pore is not in accord with the condition of continuity. For the same volume of porous material must cross each concentric spherical shell centered at any pore or at any point in the compact in the same differential time interval, during which the density is changing by the same amount throughout the compact, as he demonstrates. Hence, the velocity of any element towards the center of the shells is inversely proportional to the square of the distance. It is also inversely proportional to the density, a factor which was not left out of my equations, and appears in the function F for that reason. Dr. Shuttleworth's observer situated at the center as a pore is subject to much the same illusion as the astronomer on earth observing the recession of nebulae in an expanding universe.

G. F. HÜTTIG* (*Condensed version of translation*)—The first part of Hüttig's discussion is concerned with Shaler's distinction between "transient" and "steady state" phenomena or mechanisms in the sintering process. Hüttig considers possible different definitions of the words "mechanism" or "phenomenon," investigates whether the distinction between "steady state" and "transient" is possible on the basis of each of these definitions and comes to the conclusion that the distinction cannot be justified.

Hüttig further takes issue with Shaler's interpretation of his own theory: "I cannot agree that all the phenomena which form the basis of my theory can be considered transient for the following reasons:

"1. Even if the phenomena which I have considered are followed at higher temperature by other phenomena which complete the sintering process, this in itself would be no proof that the phenomena considered by me are transient." Hüttig argues that Shaler does not observe the final result of the sintering process, namely, a single crystal, and that it is therefore conceivable that at sintering times even longer than those employed by Shaler new phenomena are observed.

"2. It is not correct that my theory is based only on processes which are 'substantially completed in a matter of hours at temperatures considerably below those generally used in sintering.' I have taken into account all the sintering phenomena which were described in the literature up to 1941. There were 85 publications not including my own. Data on the sintering process of the metals Cu, Fe, Sn, Pb, Au, Ni, Mo, W and Al were found. Also the literature on the sintering process in oxides and other materials was collected, including data on the oxides Fe_2O_3, ZnO, BeO, CuO, Fe_3O_4, NaCl, organic materials and glasses. Of the properties by which the progress of sintering was measured, the following may be mentioned: electromotive forces, solubilities and chemical reactions with various liquid media, adsorption isotherms of methanol vapor and data calculated from them, densities in the vacuum pycnometer, apparent density, catalytic effects, electrical resistivities, gas evolution, strength, hardness, grain growth measured microscopically and by X rays, adsorption of dissolved dyes, and so on. All observations are presented in graphical form, in such a way that they can be compared with one another, in *Kolloidzeitschrift*, (1942) **98, 6–33.** On the basis of these data a theory which takes into account all the sintering phenomena was developed in *Kolloidzeitschrift*, (1942) **98,** 263–286. Other investigations based on the same methods concerned systems of two components, that is, mixtures of powders. This finally led to a theory which covers not only the sintering of single metals, but all types of chemical reactions in the solid state. These results are presented systematically in *Handbuch der Katalyse*, Vienna (1943) **VI,** 318–577.

"I wonder is it possible that a theory which takes into account such extended material can find its rightful place in Shaler's section on transient phenomena, which comprises only 34 typewritten lines."

Regardless of his criticism of Shaler's distinction between steady state and transient phenomena, Hüttig states: "The paper contains so much new material and new ideas, that I believe it may become a turning point in powder-metallurgical research. The ideas are not always easy to comprehend and the following is therefore meant more as comment than as criticism.

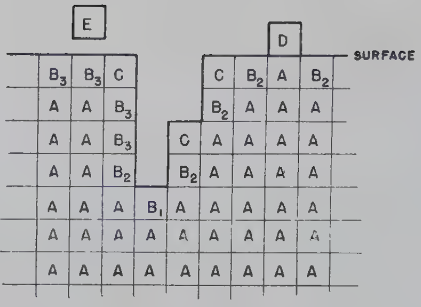

FIG 15—Representing atoms in lattice.

"1. The paper by Sackmann, Burwell and Irvine[7] is closely connected with the results of Thirsk and Whitmore (*Trans.* Faraday Soc. (1940) **36,** 862. Other papers which concern the same phenomenon are quoted in *Handbuch der Katalyse*, **VI,** 474–479 and 539–544.

"2. With regard to Shaler's concept of the electron density distribution on the surface of a metal I wonder whether the method of Grimm, Brill, Hermann and Peters who determined electronic densities by means of Fourier analysis of X ray diffraction data could not be applied also to the surface layers, perhaps on the basis of electron diffraction measurements. This may result in a direct confirmation of Shaler's concept.

"3. In order to provide experimental support to the ideas about the role which a gas plays in sintering I should like to suggest the following experiment: The progress of sintering should be investigated (*a*) in a vacuum, (*b*) under a pressure of one atmosphere, (*c*) of 10 atm. (*d*) of 100 atm. of an inert gas such as argon or helium. What differences are observed, if the other experimental conditions are held constant?

"4. I am trying to develop a simple model in order to visualize Shaler's concept of the energy and force relationships in a capillary. (Regarding the use of such models see my paper together with Joos on the energy of crystal lattices (*Ztsch. Elektrochem.* (1926) **32,** 294); W. Biltz and H. Grimm's calculation of the lattice energy of ammonia compounds (*Ztsch anorg. Chem.*, **145,** 63: and Pfeiffer and Goldschmidt's application of the idea of coordination number to the systematics of crystal lattices. Such a picture may possibly serve as a basis of discussion.

"Every atom tends towards a minimum free energy content. No important error is introduced when, in this statement, total energy is substituted for free energy. Fig 15, representing the atoms in a lattice, is drawn in two rather than in three dimensions and my discussion refers to this simplified two dimensional model. The heavy line represents a cross-section through the surface of a crystal.

"The atoms in the interior, A, have a minimum of energy. They therefore represent the most stable arrangement. All four positions of nearest neighbors are filled. Next in line with regard to increasing energy content are the B-atoms whose three nearest-neighbor positions are occupied (subdivided into B_1, B_2, B_3) then C with 2, D with one nearest-neighbor position occupied, and finally E, a freely diffusing atom with the highest energy. In a three dimensional model the coordination numbers (numbers of nearest neighbors) have to be changed accordingly.

"The surface energy is that energy which has to be expended to bring an A atom into a B position (in general a B_3 position). The same amount of energy is given off when a surface atom becomes an atom in the interior. The surface tension in dynes per cm is identical in numerical value and dimension to the surface energy in ergs per cm². The pressure which is exerted is always directed towards the mass, that is, in the direction which tends to fill the nearest neighbor positions and never in the direction of the empty space of the capillary. The entire system reaches a minimum in free energy, that is, the most stable state, when all geometrically possible movements in the sequence E-D-C-B_3-B_2-B_1-A have taken place. This process must be connected with the filling up of the capillary. All ideas which cannot be brought into agreement with this simple picture are to me very difficult to comprehend.

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5. I should like to underscore three times the sentence in the conclusion: 'The sintering process is an extremely difficult one.' "

A. J. SHALER—I thank Dr. Hüttig for his able and kind discussion, and regret that it could not be given in full. Doubtless it is dangerous, as he and others taking part in this discussion have stated, to try to dissect the interrelated parts of the sintering process without great care; it is nevertheless a very necessary part of the scientific method, and one of which Dr. Hüttig has made full use in the papers he quotes. The separation of the process into "steady state" and "transient" "mechanisms" and "phenomena" can be debated on semantic grounds, a debate which loses as much value through the imperfection of definition in our own tongue as through the additional loss of clarity attendant upon translation. That I have dealt with Dr. Hüttig's work in but a few lines in no way reflects on my part poor judgment of its importance, but rather an acceptance of the fact that he has given as final a treatment of some of the "transient" mechanisms as I had hoped to do with some of the "steady-state" phenomena. Dr. Hüttig's suggestions concerning further refinements are welcome. Some are even now being explored. His picture of the surface energy is oversimplified. It is more useful in dealing with ionic inert-gas crystals than with metals as Dr. Shuttleworth has pointed out (The Surface Energies of Inert-Gas and Ionic Crystals. *Proc.* Physical Soc. (1949) **A 62,** 167) in his statement: "In metals the surface energy is best regarded as arising from the change in kinetic energy of the free electrons due to the presence of the surface."

F. N. RHINES*—One matter that I would like to mention concerns the classification of the various steps in sintering. As a process in the scientific thinking, we very properly try to break up complex processes into small parts in order that we may look at them one at a time and thereby gain an understanding of the whole process through more simple steps. In so doing, however, I think that we should be very cautious about naming the individual steps, or about intimating that one step occurs at one time and another at another. It seems to me that the steps that Dr. Shaler has mentioned really overlap so much that all of them are going on, to some extent, most of the time. This is rather a case of one process being predominant at one moment and another being predominant later so that, perhaps, we would confuse ourselves less if we referred to the several processes without intimating so definitely that each one is associated with a specific time.

The data that I want to present are from what was to have been a paper for this meeting. Unfortunately the work was not completed in time but it is so definitely on this subject that I would like to put some of it before you.

We at Carnegie Tech have, over a period of some years, been studying the sintering process by observing the change in size and number of pores in lightly pressed compacts sintered at various temperatures and for various times in various atmospheres. I shall confine what I have to say mainly to sintering in hydrogen and at the higher temperatures, because the effects that are observed are most obvious under these conditions. Density measurements, made at intervals from 10 min. to 1000 hr at 800, 900 and 1000°C, exhibit a progressive increase, at a diminishing rate, at each temperature, the change being most rapid at 1000°C. From this observation one must conclude, as Dr. Shaler has done, that the *total volume of porosity* in the samples has been decreasing progressively. I emphasize this point to make it clear that, so far as the density measurements are concerned, there is no difference between his results and ours, because, beyond this point, our paths diverge. Our microscopic observations show very clearly that one should not further conclude that, individually, the pores are diminishing in size.

Microscope counts of the number of pores as a function of size, in single samples, show that the number rises from near zero at the smallest discernible size (of the order of 100Å in diam) to a maximum number at some intermediate size, then decreases, rapidly at first, in progressing to larger size and, then, more and more slowly, a zero number is approached just above the largest size present. With increased sintering time, the total pore count (including all sizes) diminishes and the maximum count shifts to larger pore sizes, but there is an actual increase in the number of pores of sizes greater than that at the size of the maximum count and there are a few pores of larger size than the largest observed at shorter sintering time. In other words, the larger pores are all growing at the expense of their smaller neighbors, while the smallest pores are vanishing altogether.

This is the experimental evidence. I have given just one example out of a good many that were studied, but they all follow this same pattern. We have made an effort to devise a mechanism to describe what happens to account for these observations and I would like to outline this rather briefly.

Taking a somewhat different, but I am not at all sure that it is a fundamentally different viewpoint from that of Dr. Shaler, we have assumed that the transfer of vacant space required to bring about the changes in pore diameter is accomplished by the diffusion of vacant lattice sites. We assume that the number of vacancies present in the lattice varies from place to place in the piece of metal under the influence of the surface tension at the boundaries of the pores and at the external surface. Adjacent to a small pore the number of vacant lattice sites will be large, because the higher surface tension of the small pore will increase the probability of the birth of vacancies at its bounding surface; similarly the concentration of vacancies will be less next to a large pore and still less near the external surface of the sample. This gives rise to a complex pattern of lattice vacancy concentration gradients, such that the vacant sites will tend to diffuse away from the smallest pores and toward larger pores and the external surface.

Using the surface tension value for copper, found by Udin, Shaler and Wulff, and applying conventional assumptions with regard to the variation of the lattice vacancy concentration with surface energy and with regard to the rate of diffusion of vacancies, Dr. Birchenall has succeeded in computing the change in the number of pores of each size during a stated time interval at 1000°C. His results agree very well with the observed changes. This encourages us to believe that the mechanism that I have outlined may be reasonable.

The mathematical method that Dr. Birchenall has been forced to use is, unfortunately, very cumbersome. (It is similar to the well known analysis of the growth of water droplets in equilibrium with water vapor.) For this reason, it is taking a rather long time to test the theory on all of our observations; this work is currently in progress.

I would like to add to what I have said a few comments with regard to what all this means in connection with Dr. Shaler's paper. The main conclusion that we seem to have reached is this: all except the smallest pores grow during sintering, but the rate of the disappearance of the smallest pores is such as to produce an over-all reduction in porosity. This may be hard to understand unless it is appreciated that all outdoors is a pore too and there is diffusion of vacant space into the space surrounding the sample. That is, the increase in density must be due to the diffusion of vacant lattice sites through the external surface. This would lead us to the conclusion that the rate of density change depends upon the initial number and size distribution of the pores, the amount of external surface and the thickness of the compact. I believe that it is often observed, commercially, that the smaller compacts do reach maximum density more rapidly than large compacts. My impression is that if we had a compact of infinite size the only thing that would happen would be that there would be a tendency for all the pores to agglomerate into one great big one of the same volume as the total porosity. There would be no change in density whatever. When we have an external surface some of the vacant space goes to the external surface and is lost; that gives us our densification. The more the external surface per unit of volume, the greater the rate of densification. In a compact of small size there would be, after many hours of heating, many more pores in the interior than near the surface.

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* Carnegie Institute of Technology.

Further, it seems to me that our observations are telling us that it is risky to assume, as Dr. Shaler has done in his experiments, that the pore size obtained by piling up sorted powders is really what one would compute on the assumption that there are always the same number of pores and that the change in density results from their decrease in size. I think that is not right. Some of the pores are disappearing altogether all the time, while others are growing.

Finally, I should like to make brief mention of another interesting case: that of sintering in argon. When we observe the changes in pore diameter on sintering in argon we find that, in the early stages, the process looks just like sintering in hydrogen, as described here, but at the highest temperatures and after a long time, we found a reversal in the trend of density change. That is, there was an increase in the total porosity late in the sintering process.

We think that the explanation may be this: not only must we take account of the movement of vacant space, when we are sintering in an atmosphere rather than a vacuum, but there must be movement of the gas within the metal. This is also a diffusion process, and the rate of diffusion of the gas may be quite different from the rate of diffusion of the vacant lattice sites. If the rate of diffusion of the gas is high, we may expect that the gas will get away, (disappear through the surface of the specimen), because of the squeezing down of the pores, with a consequent building up of the pressure. But if the rate of diffusion of the gas is slow, it is much less likely that the gas will reach the external surface at a rate corresponding to the change in total pore volume. Now, suppose that we transfer a given amount of gas from a given volume of little pores to the same volume of big pores. The little pores will have high surface tension; the big pores low surface tension. The little pores can sustain a higher pressure of the gas so that when the gas is moved on into the larger pores it will cause them to expand.

A. J. SHALER—We are all anxious to read the full account of the work of Drs. Rhines and Birchenall, and I am grateful to Dr. Rhines for presenting so much of it here. I should like to comment on some of the points he has made with a view to discovering if and where important differences exist between his views and mine.

I appreciate his very valid criticism of my attempt to separate the sintering process into steps, which in reality overlap one another to a great extent. In my model, which is only a first approximation to reality, two assumptions are made: (1) the pores are assumed to be far apart, and (2) they are assumed to be all of the same size. In my synthetic cylindrical pores I have tried to proceed according to the first. In the experiments on compacts I have tried to use spherical particles all of the same size in order to approach the second assumption.

F. N. RHINES—May I say, in connection with this, that you would have to be a micro-olive packer to get that condition experimentally; when you pile up spheres you are going to have some bridging, and it is inconceivable to me that, experimentally, you could even have, initially, all one size of pore; this situation would get progressively worse as you went on in sintering.

A. J. SHALER—That is correct. You have in that respect carried out the refinement, which I have not yet wanted to make, of dealing, not as I have with an impractical simple system, but with a practical and very complicated one, judging from the complexity of your equations.

The observations given by Dr. Rhines concerning the pore-size changes in copper sintered in hydrogen and in argon are not in disagreement with my results, although I have not carried out a quantitative analysis of the case of a diffusing gas —hydrogen—trapped in the pores. In both cases, the smallest pores first shrink to a small size, stable in the case of argon, but, with hydrogen, subsequently decreasing at a slower rate depending on the diffusion path of the hydrogen. At later times, successively larger pores shrink by lesser and lesser amounts. Later still, pores larger than a critical size swell instead of shrinking, and again, in argon, reach stable equilibrium sizes. In hydrogen, the swelling of pores of these sizes is followed by shrinkage as the gas diffuses out. Such developments should give the same qualitative change in pore counts as those observed by Dr. Rhines, although in my analysis I have neglected the effect on each pore of the presence of neighboring pores of greater and smaller sizes. My results indicate that, in argon sintering, there should be observed a fairly large stable pore count at very small sizes. The absence of these in Dr. Rhines' observations may be due to their being too small to be seen in the microscope; alternately, the surface tension may be sufficient to drive the residual argon into solution in the metal, notwithstanding the low solubility of this gas in copper.

F. N. RHINES—I do not think there is any evidence of a large pore count at submicroscopic size. As observed with a microscope, the pore count is decreasing at an accelerating pace all the way down to the smallest visible size. The larger pores are not shrinking; they are all growing, but the smallest pore is vanishing. I am not sure that I have got my point across yet. The point that I am trying to make and the way that I see this thing is that every pore must receive vacancy from outlying space so long as there is any pore around it that is smaller, so that we observe only growth of pores, or their total disappearance.

A. J. SHALER—Not in argon.

F. N. RHINES—No, but in hydrogen.

A. J. SHALER—The mechanism whereby pores change in size and compacts change in density by the movement of lattice vacancies is not quite the same in Dr. Rhines' view as in mine. He first establishes a gradient of vacancy concentration, then states that vacancies will diffuse down the gradient. In his treatment, as in those of Pines and Kuczynski, vacancies are treated very much as if they were atoms of matter soluble in the metal, present in mass inside the pores and outside the compact, and diffusing through the metal. Shrinkage of the compacts follows if it is shown that the vacancies are more highly "concentrated" in the small pores than in the large ones; the outlying space being the largest pore of all. Such concentration differences are ascribed to the radius-sensitivity of the pressure due to surface tension.

In my view it is not necessary to have vacancy-concentration gradients. A mechanical flow takes place by motion of vacancies under the influence of mechanical stresses due to surface tensions and gas pressures. The rate of this flow was calculated by Frenkel on the approximation that no vacancy-concentration gradients exist. In criticism of Frenkel's analysis, Nabarro (private communication) has pointed out that a single vacancy cannot be persuaded to move under a unilateral stress, but a way out of this difficulty was suggested (*Physical Rev.*, 73, 8, 926, Apr. 15, 1948).

I should like to inject a note of caution in evaluating attempts to explain mechanical behavior purely on a diffusion basis. Dissolved atoms or vacancies require an activation energy before they can diffuse. It is not sufficient, as it is in the diffusion of tenuous gases, that there be a concentration gradient. If external causes, such as the presence of surfaces of various curvatures, require local readjustments of vacancy concentration in order to minimize the free energy, then the concentration gradients are not in themselves driving forces for diffusion, because a decrease in gradient would increase the free energy. It is conceivable that a region of metal near a pore has the same flow characteristics as one far from a surface, although the former may contain many more vacancies.

It appears preferable to try to solve mechanically the mechanical problem of metal flow under stresses due to surface tension and gas pressures. The growth of large pores, which standing alone would shrink, when they are surrounded by many small ones, may be simply due to the addition of a radial tension, due to the shrinkage of the small pores, on the stress field. The system is equivalent to a hollow sphere with externally applied hydrostatic tension. That Dr. Birchenall's calculations agree well with observation is evidence that in this case the distinction between a direct mechanical solution and a diffusion solution is a semantic one only, and that our explanations are not fundamentally so different as might at first appear. The approach of Drs. Rhines and Birchenall is probably on safe ground, but that of Drs. Pines and Kuczynski is not, in my opinion, as I shall try to show in answer to the latter's remarks.

Dr. Rhines' conclusion that the rate of shrinkage depends on the size of compacts is probably true, but in both his and my model the effect must be limited to a very thin skin; it should be observable only on very tiny compacts. The commercial observations to the contrary can be better explained on the basis of the size-sensitive outward diffusion of hydrogen compressed within the pores, as described above. It should not be observed on compacts in which vacuum or a noble gas only is present within the pores.

I am happy that Dr. Rhines has found experimental evidence that pore shape has little influence on kinetics of sintering, a fact deduced theoretically in my doctoral thesis (Mass. Inst. of Technology, June 1947).

E. OROWAN*—Dr. Shaler's conclusion that the attractive force between metal surfaces has a range of several hundred Angstroms is difficult to accept. During his lecture I have calculated, on the basis of his formulas, the critical diameter for which the long-range attraction between two equal copper spheres in contact would just balance their weight; in other words, the maximum size at which we could lift up a copper sphere by means of another similar sphere in contact with it. I have repeated the calculation in another way, with the same numerical result, that is, that the critical size would be between 5 and 10 mm. If both Dr. Shaler's and my calculations were correct, therefore, metal balls of ¼ in. diam could be picked up with another similar ball as with a magnet.

A. J. SHALER—The calculation I have made for the attraction between two surfaces indicates forces greatly in excess of the technical fracture stress of copper, but not in excess of the theoretical cohesive strength calculated by the physicists for a perfect lattice. There is some experimental evidence in support of this result. Notably, Sackmann, Burwell, and Irvine (reference in paper) brought riders of copper, containing radioactive copper, gently down onto steel surfaces, and then removed them, as carefully as possible in order to prevent lateral movement. Copper could then be detected on the steel surface, indicating that the attraction between the two surfaces was greater than the fracture strength of the copper.

E. OROWAN—This can be the result of a short-range force; a short-range attraction alone, however, would not lift a copper ball by another copper ball because the force would be restricted to an extremely small circle of contact.

A. J. SHALER—I believe we are verbally performing two separate experiments. The first of these is to allow the two balls to come within a few hundred Angstroms of one another. The force of attraction will then bring the two balls into contact. The second experiment is to separate them, by allowing the weight of one to exert a tensile stress on the area of contact. As in the tensile test, the tension required to cause fracture is very low (*ca.* 10,000 psi for copper) compared with the strength of the bond between lattice nets. The reason for the discrepancy is still the subject of debate among fracture-theorists, but it may well reside in defects brought into being by plastic flow. A recent analysis and calculation made in our laboratory of a tensile test under pressure performed by Bridgman indicates that a stress of over 170,000 psi normal to an inactive slip plane was insufficient to cause fracture in copper, whereas fracture occurs in this metal when a stress of only 8500 psi is exerted in a direction normal to active slip planes. The two balls, one suspended from the other, are very much like a tensile specimen, and one would expect slip to take place first, followed by fracture at the consequently lowered stress value. The second experiment does not, then, invalidate the result of the hypothetical first experiment.

E. OROWAN—We can assume that the experiment with the two copper balls can be carried out so that there is no plastic deformation in either.

A. J. SHALER—Can we so assume? If the fracture problem were solved, I think it would be possible to analyze the problem of the two balls more adequately; I am not sure that it reduces the result of my calculation to absurdity. In the meanwhile, I should be embarrassed to have to lift one ¼ in. ball with another!

E. OROWAN—The assumption of forces that act over distances of several hundred Angstrom units is not only unlikely from the theoretical point of view; it also leads to immediate difficulties of which I have already mentioned one (the very large attractive forces that would act between spheres in contact). Another difficulty is this. When fracture occurs between two parts of a brittle solid, the work of the cohesive forces between the fragments must be of the order of the total surface energy of the surfaces of fracture. So long as these cohesive forces are small, they are determined by Hooke's law; in order to obtain the correct order of the surface energy, however, we have to assume that they cease to obey Hooke's law and begin to diminish when the increase of the atomic spacings between the two fragments becomes a substantial fraction of the initial interatomic spacing. If the cohesive forces continued to act over hundreds of Angstroms, the resulting work of separation would be several powers of 10 higher than the surface energy.

A. J. SHALER—The departure, which you describe, of the cohesive force from Hooke's law is shown by the well-known Morse curve, which is made up of a repulsive term, becoming negligible at a separation of several Angstroms, and an attractive term, extending to much greater distances. The resultant curve ceases to rise linearly and then reaches its maximum very nearly at the point where the repulsive term disappears; thereafter the contribution of the attractive force to the surface energy falls off. It is this part of the curve which I have calculated, making the usual simplifying assumptions. It may be that the surface energy calculated on this model is not so much greater than the observed value as Dr. Orowan believes. It is not possible to perform the calculation without a knowledge of the remainder of the curve.

E. OROWAN—That would amount to the assumption that the area below the Morse curve up to its maximum was a tiny fraction of the total area below the curve. This is only another way of postulating attractive forces of extremely long range.

G. C. KUCZYNSKI*—Dr. Shaler, what kind of an approximation did you use to calculate your forces?

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* Sylvania Electric Products.

A. J. SHALER—The electron density is calculated from the Fermi equation; the potential falls quadratically from a value at the surface equal to the work function.

G. C. KUCZYNSKI—I am afraid there is something wrong in these calculations. The electron wave functions do not extend very far. After few atomic distances they are overlapping and therefore the exchange forces are negligible.

A. J. SHALER—Dr. Kuczynski states that there is a considerable difference between the viscous flow mechanism and what he calls the volume diffusion mechanism. Since Frenkel's analysis is also based on volume diffusion, I fail to see how Dr. Kuczynski reaches this answer. I should like to see more of the calculation. For the coalescence of strings of spheres, treated as a one-step viscous flow process, I found an unreasonable value of the heat of activation for self-diffusion of some 30,000 cal per mol for copper. I do not see why Dr. Kuczynski should get 55,000 instead of 30,000.

G. C. KUCZYNSKI—I beg to differ with you, but the mechanism described in Frenkel's treatment of this problem is clearly stated as viscous flow and not diffusion flow.

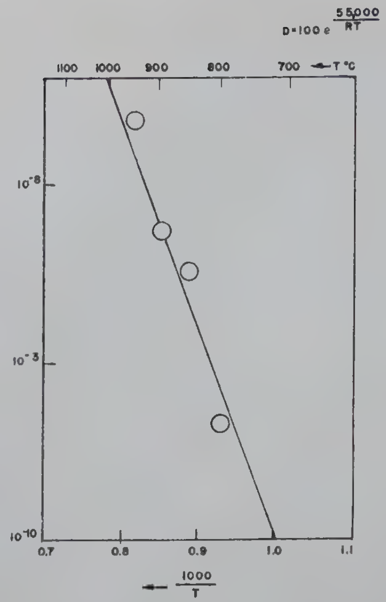

FIG 16—The variations of the coefficient of self-diffusion of copper with absolute temperature T, plotted on the semi-logarithmic scale. The points calculated from the data obtained by Dr. A. J. Shaler as represented in figure.

The difference between the viscous flow and diffusion flow mechanisms is the following: In the case of the former mechanism no concentration gradient is required. The atoms move preferably in the direction of applied stress. In the case of diffusion flow on the other hand there has to be a gradient of vacancy concentration (or interstitial atoms). These two mechanisms represent different types of flow and their rates are different.

The relationship between the radius of the interface x and time t will be:

for viscous flow — $x^2 \sim t$ and
for diffusion flow — $x^5 \sim t$

The decrease of the radius of the spherical void r with time will be:

for viscous flow — $r = r_0 - \alpha t$ and
for diffusion flow — $r^3 = r_0^3 - \beta t$

where r_0 is the original radius of the void and α, β functions of temperature only.

On the basis of the relationship for diffusion flow the heat of activation equal to 55,000 cal per mol was obtained using your data. The plot of self-diffusion coefficient as the function of $\frac{1000}{T}$ on the semi-log scale is given in Fig 16.

A. J. SHALER—My reasons for breaking the process into two steps are given in detail in the paper. These reasons are supported by the results that Dr. Duwez presented to us this morning, in which sintering-rate curves for copper could by no stretch of the imagination be extrapolated continuously to the origin; to do so may introduce an unwarranted simplification. The fact that experimental points fall more or less on a straight line when one coordinate is a high power of one of the variables is a dangerous springboard from which one can easily jump to arid conclusions.

G. C. KUCZYNSKI—There is no reason to separate your parabolic curves into two portions. If the correct functions were found, as I have shown in the case of the diffusion flow, these curves can be plotted as the straight lines which pass through the origin (Fig 17).

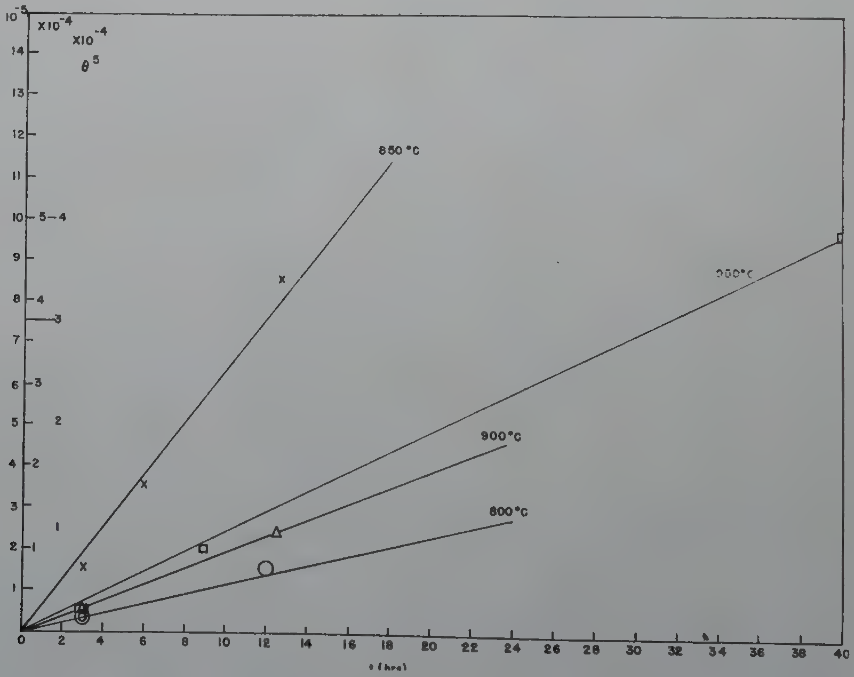

FIG 17—The plot of $\theta^5 = \left(\frac{x}{a}\right)^5$ where x is the radius of the interface and a the radius of the particles against the time of heating t in hours. The values of θ were taken from Dr. A. J. Shaler (Fig 6). It should be noted that straight lines are obtained instead of parabolic curves indicating that diffusion flow is responsible for bonding of the particles together.

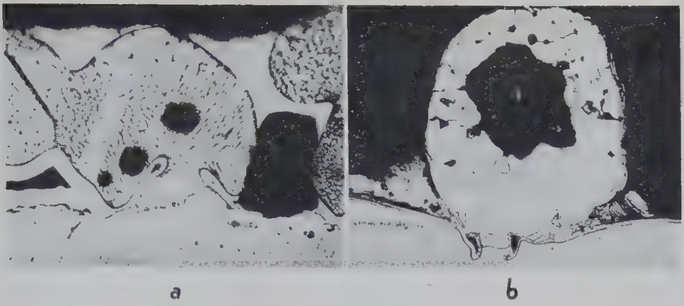

FIG 18—(*a*) Round copper particle sintered to nickel block at 950°C for 24 hr in hydrogen. Mag 700 ×. (*b*) Round nickel particle sintered to copper block at 1020°C for 48 hr in hydrogen. Mag 200 ×.

Both specimens were nickel plated after heating. Black spots inside the particles were blow holes caused by reduction of oxides in the hydrogen. Reduced one-half in reproduction.

A. J. SHALER—Dr. Kuczynski has shown a photograph of changes in shape during sintering of a copper sphere on a nickel plate, and also of a nickel sphere on a copper plate. I fail to see how these changes can help us to distinguish between a viscous flow based on diffusion or any other kind of flow based on diffusion.

G. C. KUCZYNSKI—I only showed this picture (Fig 18) to demonstrate clearly that the bonding of the metallic particles is not a result of viscous flow. Only diffusion phenomena can account for the peculiar shape of interfaces.

H. UDIN*—Dr. Kuczynski uses as a model for his sintering calculations a sphere on a plane, and then as sintering progresses material fills in at the fillet. I do not understand where this material comes from. I should like to ask Dr. Kuczynski if he is positive that his fifth power relationship comes from the actual mechanism of sintering, not from the geometry of the model.

G. C. KUCZYNSKI—Of course, the material comes from the particles.

F. N. RHINES—Do I understand that, in your derivation, you are saying that the copper that is filling these fillets is coming from the center of the sphere?

G. C. KUCZYNSKI—Some.

F. N. RHINES—You will develop a shell.

G. C. KUCZYNSKI—There will be no shell. The atoms move from the body of the particle to the "neck" and the holes are diffused out to the surface.

F. N. RHINES—Eventually you must then be taking the copper from the external surface. The question in my mind is whether you would get the same mathematical expression if you wrote it on the basis of picking your copper atoms out of the surface and transferring them through the center and out to the fillet. You seem to have left the second element of the process out of the computation, the element of moving the atom from the surface into the vacated space.

G. C. KUCZYNSKI—No, it was taken care of by the diffusion coefficient.

A. J. SHALER—In Dr. Kuczynski's model the flow of material to the neck from the surface of the particle may take place by one of two paths. Either the atoms diffuse along the surface, in which case the flow of material cannot lead to densification of the compact, but only to an increase in the area of contact (spheroidization of the pores). Or the atoms diffuse through the metal in two steps; first, along a vacancy gradient, to the neck from a region inside the particle near the neck; and, second, from the surface to that region. For the second step there exists no vacancy gradient to accelerate diffusion. It is therefore the slower and the limiting step, so that the kinetics of the process should be based on a flow mechanism requiring no vacancy gradient; that is, something similar to the viscous flow we have been discussing. Furthermore it is questionable to base the mechanism of flow even for the first step on the existence of a forced vacancy gradient; for in this case the vacancy gradient exists only in order to remove the free-energy gradient which would otherwise exist by virtue of the surface tension acting on the curved neck surfaces. A vacancy gradient alone is not sufficient for diffusion; if there is no free-energy difference between one end of the diffusion path and the other, the units of flow cannot acquire the activation energy required for motion. Therefore the first step of Dr. Kuczynski's volume diffusion process is not valid, and we must return, for a solution to the spheroidization step in sintering as well as to the densification (or swelling) stage, to a mechanical approach. In fine powders, as Dr. Kuczynski has shown, the surface-diffusion mode of spheroidization may be dominant, but densification of the compact must still occur by flow under the stresses described in my paper.

G. C. KUCZYNSKI—The process here is controlled by the slower reaction, namely self-diffusion throughout the main body of the particle. The high concentration of vacancies near the "neck" does not accelerate the rate of diffusion appreciably on the overall scale. Some variations should be noticed in the coefficient of self-diffusion (increase for the vacancy mechanism, and decrease for the interstitial atoms mechanism) during sintering of particles of only a few hundred Angstroms in diameter. But probably even in such an experiment the volume self-diffusion would be completely masked by surface diffusion.

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Relative Deoxidizing Powers of Some Deoxidizers for Steel

(With Discussion)

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Introduction

Most of the data on equilibrium constant and the deoxidations potentialities of those elements, considered to be stronger deoxidizers for steel than is silicon, have been calculated from thermodynamic data. The reason for this is, primarily, the obvious difficulty of obtaining direct experimental evidence of equivalent accuracy. This is an excellent use of the principles of thermodynamics and has given valuable data not otherwise available. Such results, of course, can be no more accurate than the physical constants used in the calculations, and one can never be sure that the basic data are either complete or accurate.

In fact, as in the case with silicon,[1] there are not only discrepancies among the calculated theoretical values of the equilibrium constant for deoxidation of steel but also between the theoretical and experimental values. It is highly desirable, therefore, to obtain experimental values for checks on calculated results whenever possible. If they disagree, both cannot be right, but if there is good agreement, their value is enhanced.

The present work was done in an effort to obtain experimental evidence in regard to some of the common alloying additions but more particularly the so-called "strong" deoxidizers for steel. The method used was to determine the minimum concentration of the deoxidizer that would effect a certain definite degree of deoxidation in steel. The criterion of deoxidation was the change from the large globular Type I sulphide to the eutectic Type II as described by Sims and Dahle.[2] This change is sharp and definite, and inasmuch as it can be produced with equal facility by aluminum, zirconium, and titanium, it is considered a manifestation of a certain degree of deoxidation and not an alloying effect.

Ostensibly such a procedure could give only a comparison of deoxidizing powers and no absolute values. Nevertheless, repeated observations have shown that, when increasing increments of aluminum are added to a steel, the residual aluminum content begins to increase simultaneously with the appearance of Type II inclusions. Thus it seems warranted to postulate that the Type II inclusions appear coincident with the virtual elimination of FeO as an active constituent of the steel.

Experimental Procedure

The data obtained were primarily from the microexamination of polished and unetched specimens and from chemical analysis. Experimental heats weighing 200 to 250 lb were made in a basic-lined high-frequency induction furnace. The base composition was nominally that of a medium-carbon casting steel to which the appropriate additions were made. Specimens were poured into sand-cast ingots 3 in. in diam as shown in Fig 1. Sand-cast ingots were used to prevent chilling and to allow sufficient time in freezing for normal inclusions to form of a size large enough to be studied readily. In the first few heats, the tapered wall ingot was used, but in the majority, the extra large riser was used to prevent piping in heavily deoxidized steels. Specimens for microexamination were taken from the location shown in Fig 1, and drillings for chemical analysis were taken from a similar location.

The procedure was to melt the base composition and deoxidize with the usual manganese and silicon additions and then to pour an ingot. The furnace was then tilted back, and the first increment of strong deoxidizer or special alloy was added and allowed to disseminate through the melt, with enough power on to hold the temperature constant, for 45 sec. Then a second ingot was poured. After this, another increment was added, and after the same holding time another ingot was poured. In this way from 9 to 12 ingots were poured from each heat, each successive ingot having progressively larger total additions of alloy.

Eighteen heats were made altogether, and the range of alloys used and additions made are outlined in Table 1. The three principal types of sulphide inclusions found are illustrated in Fig 2. The globular Type I sulphides are characteristic of silicon-killed steels, the eutectic Type II are characteristic of steels deoxidized with a small amount of aluminum, while the larger, angular Type III are usually found in steels with a residual aluminum content above about 0.02 pct.

In all specimens studied, the transition from Type I to II either did not occur at all or was very abrupt and clear cut. There never was any doubt as to just which increment produced the change, although the individual additions were small, in the order of 0.01 pct. The change from Type II to Type III was considerably less sharp, and, in some cases, both types were found together. Inasmuch as the formation of Type III sulphides is apparently not a deoxidation phenomenon, they will not be discussed here.

San Francisco Meeting, February 1949.

Any further discussion of this paper may be submitted to *Transactions* AIME as a technical note.

TP 2557 C. Manuscript received November 16, 1948; revision received July 21, 1949.

* Battelle Memorial Institute.

[1] References are at the end of the paper.

INEFFECTIVE ADDITIONS

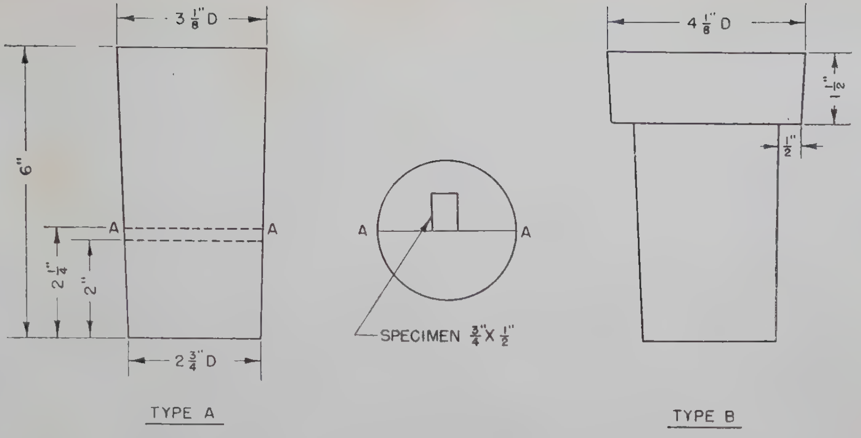

FIG 1—Sketch of experimental ingots and location of metallographic specimen.

Manganese

When manganese was varied from 0.63 pct to 17.7 pct, the globular Type I inclusions remained unchanged. In the higher manganese steels, there was a greater abundance of duplex inclusions containing both silicate and sulphide, but there was no hint of a eutectic formation. This confirms common knowledge to the effect that manganese is at best a weak deoxidizer, and that it is incapable of lowering FeO to the point that Type II inclusions can form.

It was noted that, as the manganese increased, the phosphorus content also increased from 0.009 pct to 0.040 pct, while the sulphur content decreased from 0.026 pct to 0.014 pct. The phosphorus can be accounted for as an impurity in the manganese, but the loss of sulphur is from a real desulphurizing action. This was confirmed by several analytical methods. Apparently the solubility limit for manganese sulphide was reached with high manganese contents and some manganese sulphide precipitated and floated out. It is not considered a practical desulphurization method, however.

Silicon

In Heat 1467, silicon was increased in steps up to 4 pct, but no trace of Type II inclusions was observed. Silicon is apparently a stronger deoxidizer than manganese but probably could not produce eutectic sulphides in any concentration. It was noted that the silicate inclusions increased both in size and in number as the silicon increased. They also became more transparent, indicating a higher SiO_2 content. Thus, the total silica content of the steel seemed to increase with higher silicon.

Vanadium

In Heat 1673, vanadium was added up to a content of 1 pct. The recovery of the added vanadium was practically 100 pct, indicating that it is not easily oxidized. There was no observable change in the type of sulphide inclusions. These observations plus the fact that vanadium oxide is readily reduced by silicon warrant the conclusion that vanadium has no notable deoxidizing power in steel and does not rate a position higher than silicon.

Calcium

Although calcium has been widely regarded as a deoxidizer for steel, the present tests confirmed all previous experiments of the authors in giving completely negative results. In the tests, calcium silicide was added to the bare surface of the steel in amounts up to 0.4 pct. No change in the shape of silicates or sulphides was noted, although "birds-eye" sulphides, that is, sulphides with small, round, black spots were more prevalent after the calcium additions. Spectroscopic analysis did not show any residual calcium.

Table 1 . . . Chemical Composition of Steels Studied

Heat Number	Special Element	Notes	Range in Chemical Analysis, Per Cent					
			C	Mn	P	S	Si	Al
1466	Mn	0.63/17.7 manganese	0.24/0.26	0.49/17.7	0.009/0.040	0.014/0.026	0.39/0.40	0.005/0.006
1467	Si	0.28/4.00 silicon	0.23/0.28	0.61/0.65	0.008/0.011	0.032/0.043	0.28/4.00	0.004/0.008
1673	V	0.001/1.00 vanadium	0.26/0.29	0.54/0.59	0.009/0.010	0.029/0.034	0.40/0.42	
1701	Ca	0.001/0.001 calcium	0.24/0.27	0.60/0.72	0.010	0.032/0.033	0.22/0.76	
1503	B	0.0005/0.320 boron	0.26/0.28	0.60/0.66	0.009/0.010	0.039	0.38/0.42	
1702	Mg	0.0005/0.01 magnesium	0.21/0.27	0.60/0.70	0.010/0.014	0.034/0.035	0.23/2.49	0.004/0.012
1997	Mg	0.0005/0.003 magnesium	0.30	0.69	0.006	0.045	0.66	0.003/0.005
1674	Ti	0.001/0.27 titanium	0.24/0.26	0.52/0.62	0.010/0.018	0.039	0.36/0.41	
1741	Zr	0.003/0.026 zirconium	0.32/0.33	0.62/0.65	0.010/0.011	0.037/0.038	0.25/0.34	0.006/0.008
1998	Zr	0.005/0.32 zirconium	0.34	0.71	0.008	0.018	0.30	0.003/0.005
1278	Al	Low carbon	0.08/0.10	0.38/0.43	0.017	0.033/0.034	0.17/0.21	0.003/0.237
1465	Al	Low carbon	0.06/0.08	0.61/0.63	0.008/0.012	0.041/0.045	0.40/0.44	0.006/0.17*
1279	Al	Normal carbon	0.31/0.32	0.57/0.59	0.014	0.034/0.036	0.29/0.32	0.007/0.287
1502	Al	Normal carbon	0.22/0.26	0.61/0.64	0.010	0.042/0.043	0.37/0.39	0.007/0.20*
1742	Al	Higher carbon	0.48/0.52	0.68/0.71	0.010/0.012	0.040/0.044	0.34/0.39	0.008/0.145
1502	Al	Normal Si, Mn	0.22/0.26	0.61/0.64	0.010	0.042/0.043	0.37/0.39	0.007/0.20+
1740	Al	Low silicon	0.26/0.30	0.70/0.72	0.017/0.021	0.032/0.035	0.02/0.04	0.004/0.295
1743	Al	Higher Mn	0.26/0.32	1.42/1.44	0.012/0.015	0.040/0.044	0.35/0.42	0.003/0.105
1999	Al	Higher Mn	0.31	1.47	0.009	0.039	0.32	0.003/0.86

Manganese added as an 85 pct manganese, low-carbon alloy.
Silicon added to Heat 1467 as 77 pct ferrosilicon.
Vanadium added to Heat 1673 as ferrovanadium, 51 pct vanadium.
Calcium was added to Heat 1701 as a calcium-silicon alloy to the surface of the melt.
Boron added to Heat 1503 as ferroboron.
Magnesium added to Heats 1702, 1997 in the form of a powdered iron-silicon-magnesium alloy.
Titanium was added to Heat 1674 as a pure metal powder.
Zirconium added to Heat 1741 as pure metal powder and as a silicon-zirconium alloy to 1998.
Aluminum added in the form of wire to last eight heats.
* Acid-soluble aluminum—others are total aluminum values by wet or spectrographic analysis.

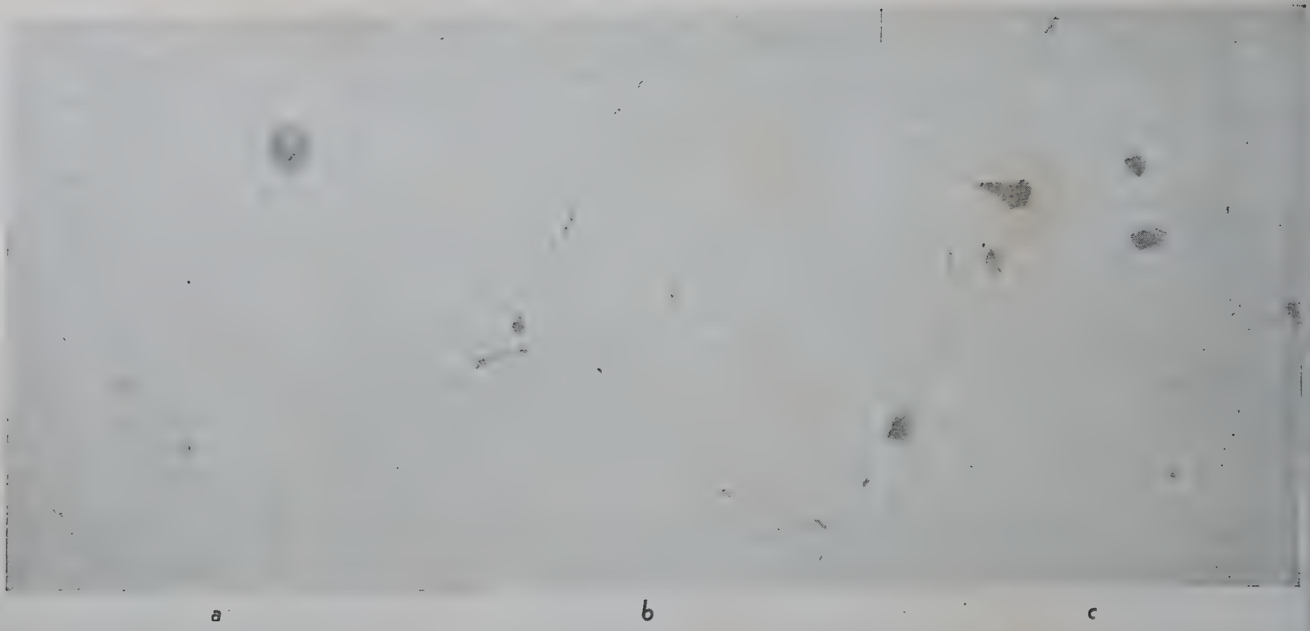

FIG 2—Typical appearance of sulphides classified on the basis of shape. 500 X.
Slightly reduced in reproduction.
a. Type I. *b*. Type II. *c*. Type III.

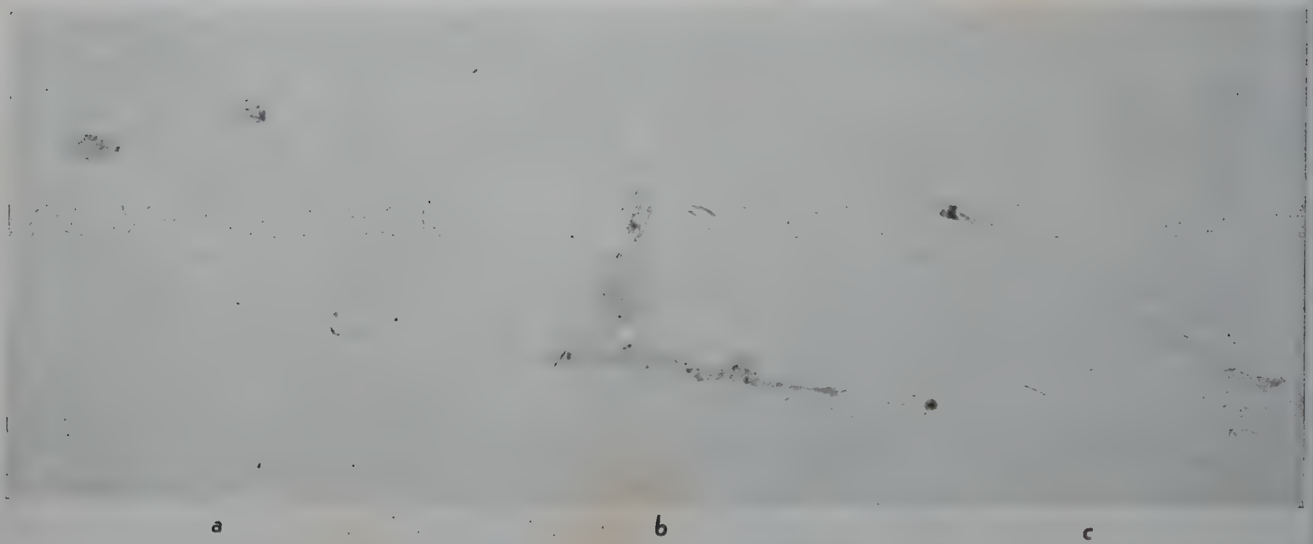

FIG 3—Typical sulphide inclusions found in Grade B steels with different boron contents. 500 X.
Slightly reduced in reproduction.
a .0.014 pct B. *b*. 0.034 pct B. *c*. 0.32 pct.

Calcium is reputedly insoluble in steel, and in molten steel, it is above its boiling point. Thus, it is under a severe handicap at best, but whether it would be a deoxidizer if it could be made to remain in contact with steel is purely hypothetical. Practically, it seems to have no deoxidizing effects.

STRONG DEOXIDIZERS

Of the elements tried, those which accomplished sufficient deoxidation to change the type of the sulphide inclusions were boron, magnesium, titanium, zirconium, and aluminum. There is some doubt regarding the deoxidation with magnesium as will be discussed later.

Boron

Boron was added to a carbon steel as 18 pct ferroboron. One effect of boron was to increase the size of the sulphides over those for similar steels containing no boron. Steels containing 0.030 pct boron, or less, were characterized by Type I sulphides and large globular silicates.

The typical sulphide inclusions in steels containing 0.034 pct or more of boron occurred as thick films in the primary grain boundaries. These inclusions have many of the characteristics of Type II sulphides in that they tend to form intergranular films, and yet they differ from those shown in Fig 2b in an important respect. Instead of being very small and forming a fairly continuous network, they are concentrated in even larger masses than the Type I and therefore will be fewer in number and further apart. For this reason, they should not have the adverse effect on ductility that usually is associated with Type II inclusions. Typical examples are shown in the micrographs of Fig 3.

Magnesium

Magnesium is similar to calcium in being insoluble in steel and in volatility. It also has a similar position in the electromotive series. In order to add it to steel, it was made up as a master alloy by dissolving it in molten 75 pct ferrosilicon to a content of 10 pct. The first such alloy also con-

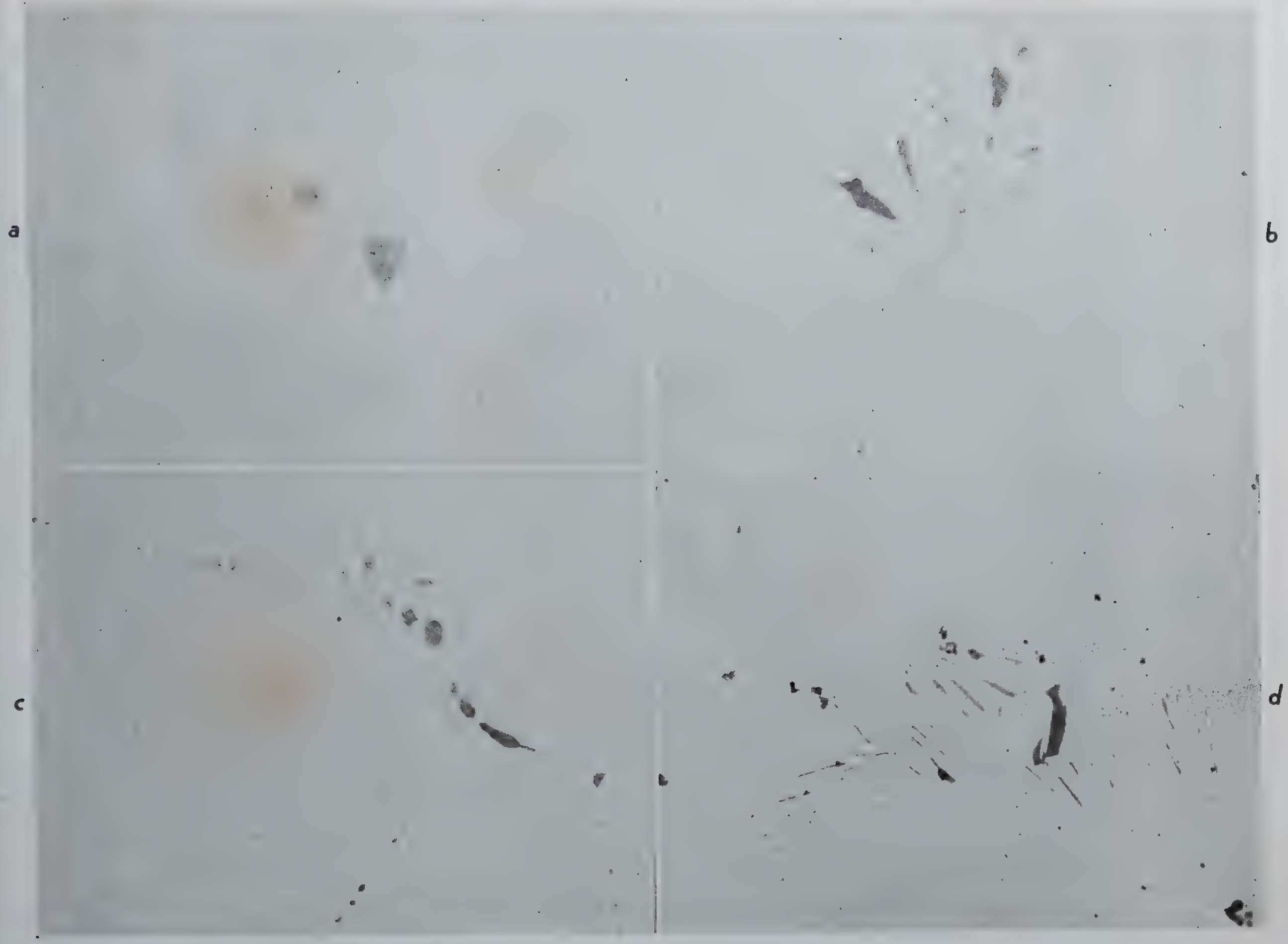

FIG 4—Typical sulphide inclusions found in Grade B steels with different titanium and magnesium additions. 500 X.
a. 0.003 pct Mg. *b.* 0.003 pct Mg, 0.005 pct Al. *c.* 0.024 pct Ti. *d.* 0.27 pct Ti.

tained 0.76 pct aluminum. When this alloy was added in increments to steel, the sulphides progressed from Type I to Type II and to Type III, the last being obtained with a total addition of 0.30 pct magnesium. Inasmuch as spectrographic analysis indicated less than 0.01 pct magnesium retained, but an aluminum content of 0.02 pct, it was considered that the latter element was responsible for the deoxidation.

Another series was made, using a similar alloy containing but 0.2 pct aluminum. The sulphides remained Type I up to a total addition of 0.30 pct magnesium at which point they changed to Type II; they remained Type II up to a total addition of 0.5 pct magnesium. Spectrographic analysis showed the residual magnesium never got higher than 0.003 pct, and the aluminum did not exceed 0.005 pct. This aluminum was high enough, however, to leave doubt as to whether the magnesium was effective as a deoxidizer.

Titanium

Titanium was added to Heat 1674 in the form of pure metal pellets placed in a hollow tube fastened on a steel rod. The tube was plunged into the bath of steel where it melted off, and the titanium was dissolved. The titanium additions were made to the furnace in amounts varying from 0.01 to a total of 0.50 pct; the recoveries ranged from 50 to 60 pct. In this series of carbon steel castings, the sulphide inclusions changed from Type I to Type II at about 0.024 pct titanium. Film or eutectic sulphides were found in all samples containing more than this amount of titanium; the last ingot showed 0.27 pct titanium by analysis. Typical micrographs of titanium-bearing steels are shown in Fig 4. Data from this series suggest that titanium contents in steels should be kept below about 0.01 pct in order to avoid embrittlement by Type II distribution of sulphides.

In the steels containing comparatively large amounts of titanium, the sulphides occurred as extremely thin films, their color tending toward tan in reflected white light. These characteristics of the sulphide inclusions were noted previously in examining a medium-manganese steel with 0.16 pct titanium which had been added as low-carbon ferrotitanium. Such sulphides are presumed to contain a large proportion of titanium sulphide.

Zirconium

A silicon-zirconium alloy was used for adding zirconium to Heat 1998 after poor recoveries resulted from using pure metal powder in an earlier trial. Seventy per cent of the zirconium present was reported as being combined with oxygen when five samples were analyzed for both total zirconium and acid-soluble zirconium. This is puzzling considering that the total zirconium contents of these samples ranged from 0.01 to 0.32 pct. If the proportion of zirconium combined with oxygen was actually quite constant. it means that the oxygen content of the steel increased or that the composition of the oxide varied. In any event, the analyses agree with the metallographic examination which showed that the quantity of oxide inclusions increased with the total zirconium contents.

The micrographs in Fig 5 show the

FIG 5—Typical sulphide inclusions found in Grade B steels with different zirconium contents and characteristic oxides in samples with large amounts of zirconium. 500 X.
a. 0.01 pct Zr. *b.* 0.03 pct Zr. *c.* 0.32 pct Zr. *d.* Oxides.

typical appearance of sulphide inclusions in three castings from the zirconium series. Eutectic film distributions existed in samples reported to contain 0.005 to 0.026 pct total zirconium. The specimen containing 0.005 pct total zirconium was found to contain 0.002 pct acid soluble zirconium and 0.003 pct was presumed to be present as oxide. Samples containing 0.03 to approximately 0.07 pct of this element were characterized by angular sulphides. As illustrated by the micrographs, the sample containing 0.32 pct zirconium indicated a reversion to film sulphides at high contents of this element. The fourth micrograph shows the inordinate number of oxide inclusions present in an ingot poured after an addition of 0.15 pct zirconium had been made to the furnace. Clouds or clusters of oxide inclusions have been found in many experimental steels treated with large quantities of zirconium. Such oxide inclusions have been determined, by electrolytic extraction followed by chemical analyses and petrographic examination, to be mainly zirconium silicate.

Aluminum

The last eight heats listed in Table 1 comprise the series made to study the effects of aluminum in steels of different compositions. The samples were analyzed for aluminum by three of the methods in common use. The first eighteen ingots were analyzed by wet methods to determine the acid-soluble and acid-insoluble (Al_2O_3) aluminum contents, because both fractions were considered important. This practice is cumbersome and occasionally gave erratic values. The spectrographic determination appeared to be much more reliable, and it is definitely faster and simpler. Only total aluminum is determined in this way, however.

Previous studies have indicated that the acid-insoluble aluminum of aluminum deoxidized steels tends to be constant, and the present data go far to verify this concept. These data for thirty samples, listed in Table 2, show that even though the total additions and the acid-soluble aluminum vary widely, the insoluble content stays close to the average value of 0.006 pct. Only three of the values varied from the average by more than 0.002 pct, and one was in a sample which contained no acid-soluble aluminum. This is within the range of precision of most wet methods of analysis. The eight heats from which these samples were taken varied in composition, but all were poured at about the same temperature of 2950°F. It appeared justifiable, therefore, to consider the insoluble aluminum a

Table 2 . . . Results of Aluminum Analyses on Test Castings

Heat Number	Ingot Number	Aluminum, Pct			
		Acid Soluble[b]	Acid Insoluble[a]	Total[d]	Added
1278	1		0.002	0.002	
	2	0.003	0.006	0.009	0.01
	3	0.003	0.006	0.009	0.02
	4	0.002	0.006	0.008	0.03
	5	0.004	0.008	0.012	0.04
	6	0.002	0.006	0.008	0.05
	7	0.023	0.008	0.031	0.075
	8	0.025	0.004	0.029	0.10
	9	0.230	0.007	0.237	0.30
1279	1	0.001	0.004	0.005	
	2	0.001	0.005	0.006	0.01
	3	0.002	0.007	0.009	0.02
	4	0.008	0.005	0.013	0.03
	5	0.007	0.006	0.013	0.04
	6	0.015	0.004	0.019	0.05
	7	0.027	0.004	0.031	0.075
	8	0.041	0.005	0.046	0.10
	9	0.280	0.007	0.287	0.30
1465	12	0.17	0.005	0.175	0.30
1502	10	0.13	0.006	0.136	0.175
		Acid Soluble[d]		Total[c]	
1999	5	0.018	0.007	0.025	0.05
	10	0.34	0.005	0.34	0.40
	12	0.85	0.006	0.86	1.00
1743	9	0.049	0.010	0.059	0.15
	6	0.006	0.008	0.014	0.05
1742	12	0.137	0.008	0.145	0.30
1740	11	0.213	0.007	0.220	0.40
	7	0.067	0.006	0.073	0.15
	5	0.025	0.007	0.032	0.08
	3	0.007	0.012	0.014	0.04
			Avg. 0.0062		

[a] Insoluble residue in wet analysis considered as Al_2O_3.
[b] Acid-soluble aluminum value from wet analyses.
[c] Total aluminum determined by spectrographic analysis.
[d] Calculated from other two results.

Table 3 . . . The Relation Between Content of Deoxidizer and Formation of Eutectic Sulphides

Heat No.	C	Mn	Si	S	P
A 1503	0.26	0.64	0.42	0.039	0.010

Total Boron Content	0.0005	0.006	0.014	0.023	0.032	0.041	0.058	0.062
Inclusion Type	I	I	I	I	II	II	II	II

Heat No.	C	Mn	Si	S	P
A 1674	0.26	0.59	0.36	0.039	0.018

Total Titanium Content	0.015	0.020	0.024	0.037	0.05
Inclusion Type	I	I	II	II	II

Heat No.	C	Mn	Si	S	P
A 1741 A 1998	0.33 0.34	0.62 0.71	0.32 0.30	0.038 0.018	0.011 0.008

Zirconium* Content	0	0.002	0.002	0.008	0.010	0.014	0.022	0.026
Inclusion Type	I	II	II	II	II	II	II	II

* First two are acid-soluble Zr, rest total Zr.

Heat No.	C	Mn	Si	S	P
A 1278 A 1465	0.09 0.07	0.41 0.63	0.18 0.41	0.033 0.045	0.017 0.011

Residual Aluminum	0.002	0.003	0.004	0.005	0.006	0.008	0.011	0.023	0.024	0.025	0.037
Inclusion Type	I	I	I	I	I	I	II	II	II	II	II
Res. Al	0.053										
Inc. Type	II										

Heat No.	C	Mn	Si	S	P
A 1279 A 1502	0.32 0.24	0.58 0.63	0.29 0.38	0.035 0.042	0.014 0.010

Residual Aluminum	0.002	0.002	0.005	0.007	0.008	0.014
Inclusion Type	I	II	I & II	II	II	II

Heat No.	C	Mn	Si	S	P
A 1742	0.51	0.69	0.36	0.043	0.011

Residual Aluminum	0.003	0.007	0.014	0.019
Inclusion Type	I	II	II	II

Heat No.	C	Mn	Si	S	P
A 1740	0.30	0.72	0.04	0.033	0.020

Residual Aluminum	0.002	0.009	0.015	0.027	0.035	0.066
Inclusion Type	II	II	II	II	II	II

Heat No.	C	Mn	Si	S	P
A 1743 A 1999	0.30 0.31	1.43 1.47	0.36 0.32	0.041 0.039	0.012 0.009

Residual Aluminum	0.002	0.003	0.004
Inclusion Type	II	II	II

constant at 0.006 pct and to simplify the determination by wet analysis for soluble aluminum only, or to use the spectrographic method and subtract 0.006 pct from the total.

In the different heats, residual aluminum contents, varying from 0.002 to 0.005 pct, were required to initiate the formation of eutectic sulphides in the various steels except for the two low-carbon Heats Al278 and Al465. In these steels, Type I sulphides persisted with an aluminum content of 0.008 pct. The Type III, angular sulphides, were readily obtained with aluminum contents of about 0.015 pct or more with all steels except those very low in silicon or carbon.

COMPARISON OF DEOXIDIZERS

Only those elements which can lower the FeO content enough to cause formation of Type II sulphides are amenable to comparison by the presently proposed method. The elements tested which fall into this category are aluminum, zirconium, titanium, and boron. None of the others apparently is a stronger deoxidizer than silicon.

The pertinent analytical data for the stronger elements are given in Table 3; and in Fig 6 there is a graphic representation of the quantity in the steel necessary to change the sulphides to the Type II. It will be noted that

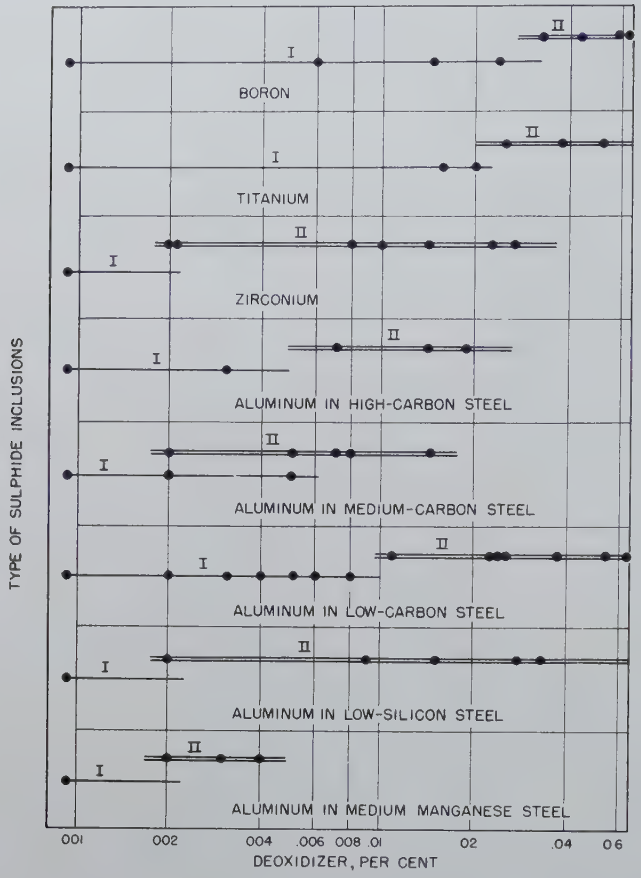

FIG 6—Showing relation between content of deoxidizing element and change to eutectic sulphide.

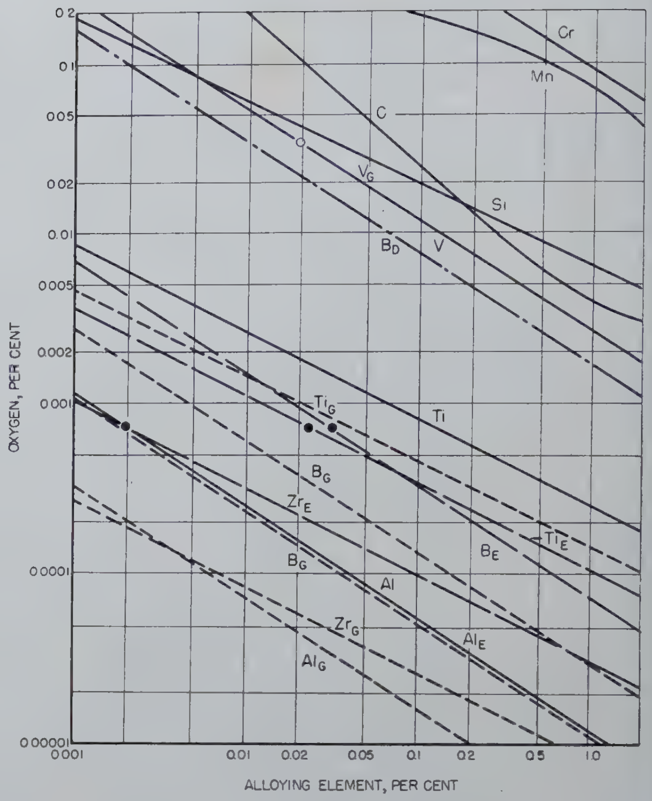

FIG 7—Comparison of deoxidizing powers at 2900°F (1600°C) for calculated and experimental values.

Solid lines Chipman's calculated values. Subscript E refers to present experimental work; subscript G refers to Gurry's calculated values; subscript D refers to Derge's experimental value.

for aluminum the change took place with a residual content of 0.002 pct for three cases, but in the steels containing 0.07 and 0.09 pct carbon, it required about 0.01 pct. In the high-carbon steel (0.51 pct C), the transition is a bit uncertain, but there was no change at 0.003 pct aluminum.

With zirconium, the transition was definite at a residual content of 0.002 pct which places it at least the equal of aluminum. In the case of titanium and boron, no distinction was made between soluble and insoluble portions, and the values given are determinations of total contents. From these it is deduced that they are considerably weaker than aluminum and zirconium.

For comparison with calculated values, the experimental values for the medium carbon steels are superimposed on Chipman's chart as it appears in "Basic Open Hearth Steelmaking," 1944, p. 498, in Fig 7. No absolute values were obtained in the experimental work, and Chipman's value for aluminum was chosen as the standard, and the experimental value for aluminum made to coincide with it. Gurry's[3] calculated values for aluminum, zirconium, titanium, boron, and vanadium are also plotted as is Derge's[4] experimental value for boron. The experimental values for titanium and boron are plotted on the basis that oxygen level is the same in all steels, regardless of deoxidizer, at the transition from Type I to Type II sulphides.

It is notable that Gurry's values for aluminum and zirconium have nearly the same relation to each other as the experimental values, but Gurry's figure for aluminum is much lower than Chipman's (stronger deoxidizer). The experimental value for titanium is lower than both Chipman's and Gurry's calculated values but is quite close to the latter. The experimental value for boron is definitely higher than either of Gurry's calculated values but also much lower than Derge's experimental value. Chipman's and Gurry's values for vanadium coincide.

SIGNIFICANCE OF THE ANALYSIS FOR ALUMINUM

One of the difficulties in obtaining data on the deoxidation with aluminum is that the limit of accuracy for analytical methods is reached for the very low values of aluminum. The values in Table 2 were carefully checked by a skilled analyst and are believed to be accurate within the limits of the method used.* The acid-insoluble portion of the aluminum is generally believed to be present as Al_2O_3, and in aluminum deoxidized steels, inclusions can be seen which are identifiable as Al_2O_3 and which seem to agree in quantity with the analytical results.

It has been tacitly assumed and widely believed that, when aluminum is added to steel, part of it is oxidized to Al_2O_3 (the deoxidation reaction), and that the solubility of Al_2O_3 being virtually nil, this Al_2O_3 is instantly precipitated. Much of it floats to the surface of the liquid steel, but some of it, because of its small particle size, remains suspended and is trapped when the steel freezes. Such a belief appears untenable in the face of the present data.

The constancy of the value for insoluble aluminum in steel, as shown in Table 2, has been noted before. Sims and Dahle[2] reported somewhat higher values. Halley[5] analyzed some steels deoxidized with aluminum in large-sized commercial molds and obtained results as follow:

---

* Insoluble aluminum separated by acid digestion, fused in potassium bisulphate, dissolved in dilute H_2SO_4, and electrolysed on a mercury cathode. The aluminum is precipitated from this solution and determined as Al_2O_3.

Acid-soluble Aluminum	Al_2O_3	Insoluble Aluminum
	0.001	0.0005
0.001	0.008	0.004
0.009	0.008	0.004
0.038	0.008	0.004
0.073	0.010	0.005
0.169	0.008	0.004

Wentrup and Hieber[6] gave analyses of 40 experimental low-carbon steels deoxidized with aluminum and with residual aluminum contents that ranged up to 0.83 pct. In 38 of these he obtained contents of acid-insoluble aluminum ranging from 0.001 to 0.012 pct with an average value of 0.005 pct. This is a significant corroboration and is considered to verify, first, that the insoluble aluminum tends to have a constant value and, second, that this value is in the neighborhood of 0.004 to 0.006 pct.

The constancy of this Al_2O_3 content cannot be accounted for on the basis that it was just the residue that failed to float out of the steel while it was still liquid. The recovery of added aluminum seldom is much higher than about 50 pct, and, in the case of a 4 lb per ton addition, the oxidized aluminum would be in the amount of 0.2 pct or thirty times the amount found in the solidified steel. If it is all precipitated, in varying amounts, why should an amount so constant remain suspended?

It cannot be accounted for as the Al_2O_3 that precipitates as a result of the shift in equilibrium constant during cooling of the steel to the freezing temperature, because the amount of oxygen involved is upwards of ten times the amount available from this source on the basis of Chipman's calculated value at 1600°C or thirty times what Gurry's value would allow, as shown in Fig 7.

The only logical explanation seems to be that the Al_2O_3 found in the solid steel was actually in solution in some form in the liquid steel and precipitated during cooling and freezing. Moreover, it was a saturated solution in the liquid steel which accounted for the constancy. All oxide above the saturation value was precipitated instantly and floated out rapidly. The slight difference between the average value for acid-insoluble aluminum in Table 2 and Halley's value could then be due to temperature, because his heats were probably poured at about 2800°F (1550°C); whereas, the heats of Table 2 were poured in the range of 2900 to 2950°F or a little over 1600°C. The solubility would be expected to be higher at the higher temperature.

It still remains to account for this solubility in the light of physical-chemical concepts.

A TENTATIVE THEORY ON THE DEOXIDATION REACTION AND THE FORMATION OF OXIDE INCLUSIONS

A tentative theory to account for the presence of the Al_2O_3 in solidified steel proposes that the deoxidizing reaction is first of all a homogeneous reaction in which the dissolved deoxidizing element "M" reacts with dissolved FeO in the steel to partition the oxygen and to form a monoxide of the deoxidizer. The reaction is

$$[FeO] + [M] \rightleftharpoons Fe + [MO] \qquad [1]$$

and the equilibrium constant for the reaction is

$$K_{MO} = \frac{\%\ Fe \times \%\ MO}{\%\ FeO \times \%\ M} \qquad [2]$$

The MO formed has a limited solubility which varies with the concentration of M. Any excess of the MO over the solubility limit is quickly precipitated and rejected to the slag. During, or subsequent to, the precipitation, the MO disproportionates to form a higher oxide by such a reaction as

$$2\ MO \rightleftharpoons MO_2 + M \qquad [3]$$

$$3\ MO \rightleftharpoons M_2O_3 + M \qquad [4]$$

or

$$Fe + 4\ MO \rightleftharpoons FeO{\cdot}M_2O_3 + 2\ M. \qquad [5]$$

The disproportionation reaction may be simultaneous with the precipitation in some cases so that actually no MO exists as a separate phase, in which case it would be indistinguishable from direct precipitation of the higher oxide, or, on the other hand, it may be delayed in other systems, possibly requiring lower temperatures for completion. The presence of two oxides in the external phase, one of which is also in solution, would appear to violate the phase rule. For example, in Eq 3 to 5 above, there are two components and two phases which, at constant pressure, allow only one degree of freedom. This would mean that two solid oxides could exist at only one set of conditions (temperature, pressure, and composition). A way to avoid this objection is indicated by Willis,[7] who postulates that oxides in contact with molten metals cannot be regarded as classic stoichiometric compounds. For example, Wüstite, ostensibly FeO, has been found to contain too much oxygen for this composition. It cannot be regarded as a solid solution of Fe_2O_3 in FeO, because in the space lattice of the solid, there are no molecules let alone molecules of Fe_2O_3. It can be regarded only as a nonstoichiometric oxide. It seems possible, therefore, to have an oxide equivalent to MO plus M_2O_3 existing as a nonstoichiometric compound.

The importance of this to the present concept seems evident in the following quotation from Willis.[7] "Since the composition of a nonstoichiometric compound is dependent on both temperature and the partial pressure of one of the components, any such compound must be regarded as a two-component system, where the classical compound of fixed composition represents only one component. In equilibria, involving variability of composition of a compound, an extra degree of freedom is introduced above those which would be found when the compound is counted as a single component."

Chipman[8] has given good evidence that oxygen in liquid iron exists as a compound having one atom of oxygen, which for simplicity is assumed to be FeO. Fontana and Chipman[9] later showed that when iron becomes saturated with FeO, as by cooling or freezing, FeO is precipitated. As the temperature falls, the FeO becomes less stable and partially disproportionates by the reaction

$$4\ FeO \rightleftharpoons Fe_3O_4 + Fe. \qquad [6]$$

At any rate, some Fe_3O_4 is produced as a separate phase, and some islands of Fe can be observed in the Fe_3O_4. Although no deoxidation reaction is involved, the case is analogous and represents a condition in which the disproportionation to a higher oxide form is not complete even at room temperature.

Zapffe and Sims[1] contended that SiO must play an important part in the silicon deoxidation of steel and gave some visual evidence that SiO might precipitate first and then decompose to SiO_2 plus Si. The disproportion of SiO is apparently very fast, however, and shows only in rapidly chilled specimens. Zapffe[10] later elaborated this thesis with considerable additional evidence. He showed, for example, evidence of the silicon-enriched concentric envelope around the silica inclusion, which

Table 3 . . . Limiting Gas Compositions and Oxygen Content in Chromium-iron Alloys in Equilibrium with Chromium Refractories, Taken from Table VI of Chen and Chipman[11] With Calculated Values Showing Partition of Oxygen and the Constant for the Homogeneous Equilibrium

$\frac{H_2O}{H_2}$	Cr, pct	Total O_2, pct	O_{Fe}, pct	O_{Cr}, pct	FeO, pct	CrO, pct	$K_3 = \frac{CrO \times Fe}{FeO \times Cr}$
0.162	1.0	0.045	0.0387	0.0061	0.174	0.0261	14.8
0.116	2.0	0.036	0.0272	0.0088	0.124	0.0374	14.8
0.081	4.0	0.031	0.0188	0.0123	0.0845	0.0522	14.8
0.070	5.5	0.030	0.0160	0.0146	0.0720	0.0620	14.8
0.056	8.0	0.029	0.0124	0.0170	0.0060	0.0722	14.8
0.046	10.0	0.028	0.0100	0.0175	0.0450	0.0742	14.8
0.041	12.0	0.027	0.0087	0.0187	0.0392	0.0793	14.8
0.034	16.0	0.027	0.0069	0.0206	0.0310	0.0878	14.9
0.029	20.0	0.027	0.0059	0.0220	0.0252	0.0935	14.8

would be the logical resultant of such a reaction.

In the carbon-oxygen reaction in steel, CO is formed and evolved (precipitated) as a gas. This gas always contains an equilibrium content of CO_2 which may be considered to have formed by the reaction

$$2\ CO \leftrightharpoons CO_2 + C \qquad [7]$$

Chen and Chipman[11] give excellent reasons to believe that, in the Cr-O equilibrium in liquid iron, the oxygen is partitioned between FeO and CrO in a ratio that varies with Cr content. The only oxide inclusions found in the solidified Fe-Cr alloys, however, were chromite, FeO Cr_2O_3, for those alloys containing up to 5.5 pct Cr, and chromic oxide, Cr_2O_3, in those of higher Cr content. Many of these chromite or chromic oxide inclusions contained islands of metal in a dendritic pattern. This fits very well into the picture of CrO precipitating and disproportionating as

$$3\ CrO \leftrightharpoons Cr_2O_3 + Cr \qquad [8]$$

or

$$4\ CrO + Fe \leftrightharpoons FeO{\cdot}Cr_2O_3 + 2\ Cr \qquad [9]$$

but gives no evidence that CrO ever existed as a separate phase.

Zapffe, in discussing the paper by Chen and Chipman's, argued strongly for the formation of Cr_2O_3 by the disproportionation of CrO, but he made a better case in his own paper.[10]

Some evidence for the existence of CrO as a separate phase in chromium alloys was obtained by Elsea, Westerman, and Manning.[12] High-chromium alloys, melted in an argon atmosphere, were found to be very high in inclusions of Cr_2O_3 when beryllia crucibles were used. When alumina crucibles were used, however, the alloys were practically free of oxide inclusions, but the crucibles had high contents of $CrO{\cdot}Al_2O_3$ spinel. The CrO had obviously come out of the alloy as such and had combined with the alumina at the high temperature where the CrO is more stable.

Hilty[15] has given very convincing evidence that in the simultaneous oxidation of carbon and chromium, from an alloy of iron, carbon and chromium, the oxides involved in the reaction are CO and CrO and that the reaction is

$$CrO + C \leftrightharpoons Cr + CO.$$

On the postulate that, in alloys containing up to 5.5 pct Cr, precipitated CrO disproportionates to form chromite according to Eq 9, then

$$K_1 = \frac{[\%\ Cr]^2}{[Fe][CrO]^4}. \qquad [10]$$

Since this is a heterogeneous reaction, the K_1 is really a steady state constant, but it can be treated as an equilibrium constant providing the same standard states are used for any given substance in all parts of the system. On the premise that the concentration of iron is nearly constant for such alloys, [CrO] content should be approximately proportional to the square root of [Cr]. For the higher chromium alloys, if CrO breaks down to chromic oxide according to Eq 8, then

$$K_2 = \frac{[\%\ Cr]}{[CrO^3]} \qquad [11]$$

and the concentration of [CrO] should vary as the cube root of [Cr].

In Table 3 is listed the limiting oxygen content of alloys, containing up to 20 pct Cr, which are in equilibrium with chromite or chromic oxide at 1595°C and the gas compositions with which they would also be in equilibrium. These values were taken from Table 6 of Chen and Chipman.[11] In addition, values for O_{Fe}, O_{Cr}, FeO, and CrO are given which were calculated by the following formulas developed by those authors:

$$[\%\ O_{Fe}] = 0.241 \left(\frac{H_2O}{H_2}\right) \frac{\%\ Fe}{100}$$

$$[\%\ O_{Cr}] = 3.79 \left(\frac{H_2O}{H_2}\right) \frac{\%\ Cr}{100}.$$

The equation for [% O_{Fe}] was developed from data obtained on pure iron, whereas the formula for [% O_{Cr}] was obtained by subtracting the first equation from one for total oxygen.

In Fig 8, the values of CrO are plotted against the square root of Cr contents for alloys containing up to 5.5 pct Cr and against the cube root of Cr content for alloys containing from 5.5 to 20 pct Cr. It will be noted that acceptably straight lines, showing direct proportionality, were obtained. This gives considerable support to the postulate regarding CrO.

Table 3 also shows that the equilibrium constant for the homogeneous equilibrium

$$[FeO] + [Cr] \leftrightharpoons [CrO] + [Fe] \quad [12]$$

which is

$$K_3 = \frac{[CrO] \times [Fe]}{[FeO] \times [Cr]} = 14.8 \quad [13]$$

does not vary in the range 1 to 20 pct Cr. It also remains constant when [Cr] or total [O] are below the limiting values or saturation point.

This concept does not appear to violate the heterogeneous equilibrium of the chromium-iron alloys with chromite in one case and with chromic oxide in the other, as shown so well by Fig 10 of Chen and Chipman.[11] These higher oxides, or oxides of closely similar oxygen contents, furnish the oxygen pressure that determines the oxygen content of the alloys.

Abundant evidence has been brought forth recently to establish the knowledge that lower valence compounds of aluminum, zirconium, titanium, silicon, and chromium are stable at high temperatures under favorable (reducing) conditions. The production of ductile zirconium and titanium by the hot-wire iodide method depends, in part, on the formation of low-valence iodides which disproportionate to higher valence iodides and metal at high temperatures. Aluminum can be distilled by heating a mixture of the metal and AlF_3. The reaction $2Al + AlF_3 \leftrightharpoons 3\ AlF$ is reversible with appropriate changes in temperature and the AlF is volatile. The reaction $Si + SiO_2 \leftrightharpoons SiO$ is used to produce volatile SiO to coat mirrors. When present in a slag, TiO_2 is an excellent flux, but under reducing conditions, it goes to a lower oxide and produces a viscous slag.

Alumina heated in vacuo at 1800°C with metallic silicon was reduced to products identified as SiO and (probably) Al_2O.[13] AlO has been identified definitely in the spectrum of gases at high temperature.[14] When Al_2O_3 is heated in vacuo with metallic Ti or ZrO_2 with metallic Al, these refractory substances are disintegrated by the formation of suboxides

$$Al_2O_3 + Ti \rightleftharpoons 2\ AlO + TiO$$
$$ZrO_2 + Al \rightleftharpoons ZrO + AlO.$$

Apparently these reactions are typical and common.

THE ALUMINUM-OXYGEN EQUILIBRIUM

Evidence has been given to the effect that the alumina* found in solidified steels, which have had at least a short interval of time in the liquid state after deoxidation, represents material that was in solution while the steel was molten, and that the oxygen in this alumina far exceeds that permitted by the calculated deoxidation constants. The difference seems to be something more than experimental error.

To obtain further data, specimens having a wide variation in residual aluminum content were selected from those shown in Table 2 and were analyzed for total oxygen by the vacuum fusion analysis method, using a technique which has been shown to have a precision of ±0.0004 pct O_2. The results are shown in Table 4.

Table 4 . . . Specimens Selected for Determination of Total Oxygen by Vacuum Fusion. The Corrected Value for Acid-insoluble Aluminum is Based on the Belief that the Average Value for this Constituent Shown in Table 2 is More Reliable than Individual Determinations. The Analyses for Oxygen are Typical of Many which Have Been Made on Aluminum Deoxidized Steels

Sample Number	Acid-Soluble Aluminum	Insoluble Aluminum		Total Oxygen
		Analyzed	Corrected	
1279–1*	0.001	0.004	.....	0.019
1279–3	0.002	0.007	0.006	0.008
1279–5	0.007	0.006	0.006	0.006
1279–6	0.015	0.004	0.006	0.005
1279–7	0.027	0.004	0.006	0.005
1279–8	0.041	0.005	0.006	0.005
1502–10	0.13	0.006	0.006	0.005
1465–12	0.17	0.005	0.006	0.005
1279–9	0.28	0.007	0.006	0.005

* No Al added.

Most outstanding is the fact that total oxygen decreases with increasing residual aluminum but only to a minimum value of 0.005 pct. For 0.006 pct Al as Al_2O_3, the stoichiometric value for oxygen would be 0.0053 pct which is well within the precision of the analytical methods. Thus, it appears that practically all of the oxygen is present as Al_2O_3 in solid steels containing as much as 0.015 pct residual Al. With contents of 0.007 pct residual Al, there is presumably some oxygen present as FeO.

According to this new concept, the deoxidation reaction is

$$[FeO] + [Al] \rightleftharpoons [AlO] + [Fe].$$

Any AlO in excess of the solubility for the temperature is precipitated and disproportionates as

$$3\ AlO \rightleftharpoons Al_2O_3 + Al$$

or

$$Fe + 4\ AlO \rightleftharpoons FeO{\cdot}Al_2O_3 + 2\ Al.$$

This material quickly rises out of liquid steel. The soluble portion of the AlO precipitates during cooling and freezing and forms the familiar inclusions found in aluminum deoxidized steels.

The apparent constancy of Al_2O_3 in the solid steel, which infers a similar constancy of AlO in the liquid steel, would seem to violate the theory expounded on page 821, which stipulates that AlO should vary as some function of the Al content. The typical deoxidation curve (oxygen vs. deoxidizer), however, is roughly an hyperbola and, after a certain content of deoxidizer is reached, the curve becomes nearly horizontal. With such a strong deoxidizer as aluminum, this nearly horizontal portion is quickly reached. Here the bulk of the oxygen is present as Al_2O_3, and although the content is theoretically not constant, the variation is too slight to be detected by present analytical procedures and, for purposes of calculation it may be considered constant without introducing a significant error.

The equilibrium constant can be expressed as

$$\frac{[FeO] \times [Al]}{[AlO] \times Fe} = K, \qquad [13]$$

but since the [AlO] and Fe are nearly constant for a wide range of aluminum contents, it may be simplified to

$$[FeO] \times [Al] = K. \qquad [14]$$

The constant quantity of 0.006 pct acid-insoluble aluminum can be calculated to 0.0143 pct AlO in the liquid steel. This would liberate 0.003 pct Al, most of which should be available as acid soluble, when it goes to the higher oxide form.

Using the meager data of Table 4, the values for Sample 1279-5 give

$$[O_{FeO}] = [O_T] - [O_{AlO}]$$
$$= 0.006 - 0.0053 = 0.0007 \text{ pct} \qquad [15]$$
$$[FeO] = 0.00315 \text{ pct} \qquad [16]$$
$$^*[Al_R] = Al_S - Al_L$$
$$- 0.007 - 0.003 = 0.004 \text{ pct} \qquad [17]$$
$$K = [FeO] \times [Al] = 0.00315 \times 0.004$$
$$= 1.26 \times 10^{-5} \qquad [18]$$

The best test for this constant is to see whether it can predict other conditions. In the case of Sample 1279-3, if the values 0.006 pct for insoluble Al and 0.008 pct for total O_2 are used with this value of K to calculate the residual Al, the figure of 0.004 is obtained compared with the analyzed value of 0.002 pct. For Sample 1279-6, if the values 0.006 pct for insoluble Al and 0.015 pct for soluble Al are used to calculate the oxygen present as FeO, the figure 0.00022 pct is obtained. This gives a total oxygen of 0.00552 pct as compared with the analytical value of 0.005 pct. The coincidence of the calculated and analyzed values is well within the limits of precision of the analytical methods. The quantities of FeO become unmeasurably small for still higher aluminum contents.

Because of the obvious limitations of analytical accuracy in this range, the deoxidation constant for aluminum cannot be regarded as highly accurate. The 1.26 calculated might be as low as 0.5 or as high as 2.5, but it is believed to be in the correct degree of magnitude. Total oxygen, for any given residual aluminum content, calculated from this constant, falls very close to analytical results, in contrast to previously calculated values for the deoxidation constant, as shown above.

THE ZIRCONIUM-OXYGEN EQUILIBRIUM

Data were given earlier (p. 817) to indicate that, in a steel deoxidized with silicon and zirconium, approximately 70 pct of the zirconium was present in acid-insoluble form. This was true over a range of total zirconium from 0.01 to 0.32 pct. If it be assumed that the insoluble zirconium represents oxidized zirconium (the nonmetallic inclusions seemed to be largely zirconium silicate), then it must be presumed that some form of zirconium oxide, probably ZrO, has a high solubility in liquid steel and that this solubility varies with the content of residual or unoxidized zirconium. Tentatively, at least, this fits in very well with the presently postulated theory.

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* This does not, naturally, include those streaks of aluminous inclusions found near the surface of ingots and which usually represent occluded scum.

* R = residual Al in liquid steel
S = acid soluble
L = liberated by disproportionation

NOTES ON THE CHROMIUM-OXYGEN EQUILIBRIUM

When chromium is used as a deoxidizer, some chromium oxide will be precipitated, leaving some CrO in solution. The metal will, of course, be in equilibrium with the precipitated oxide and the values of dissolved CrO (when at 1595°C) can be taken from the curves of Fig 8. From these the following constants are obtained:

For contents up to 5.5 pct Cr

$$K_1 = \frac{(\%\ \mathrm{Cr})^{1/2}}{\mathrm{CrO}} = 38.4$$

$$[\mathrm{CrO}] = \frac{(\%\ \mathrm{Cr})^{1/2}}{38.4} = 0.026\ (\%\ \mathrm{Cr})^{1/2}$$

For contents of 5.5 to 20 pct Cr

$$K_2 = \frac{(\%\ \mathrm{Cr})^{1/3}}{\mathrm{CrO}} = 29.0$$

$$[\mathrm{CrO}] = \frac{(\%\ \mathrm{Cr})^{1/3}}{29} = 0.0345\ (\%\ \mathrm{Cr})^{1/3}.$$

By substituting the value for [CrO] in the equation

$$K_3 = \frac{[\mathrm{CrO}] \times \mathrm{Fe}}{[\mathrm{FeO}] \times [\mathrm{Cr}]} = 14.8$$

the [FeO] content may be calculated. The total oxygen is then readily obtained.

It will be noted here that no activity coefficients are used and that all components are assumed to have an activity proportional to concentration. This illustrates the postulate of some physical chemists who contend that most materials at very high temperatures have activities proportional to their concentration and that, if the correct chemical species are known and used, activity coefficients, which are really correction factors, are unnecessary.

Very pertinent to the foregoing discussion is the fact that the data for $[O_{Fe}]$ also represent the activity of oxygen in the iron-chromium alloys, or $a_0 = [O_{Fe}]$. The activity coefficients reported by Chen and Chipman[11] may be obtained as the ratio of $[O_{Fe}]$ to total [O] or $\frac{[O_{Fe}]}{[O_{\mathrm{total}}]} = f_0$.

Summary

In experimental work to test the deoxidizing powers of commonly available elements, manganese, vanadium, and calcium were found to be no stronger than silicon. None of these is able to reduce the FeO content of steel sufficiently to form No. II type sulphides. Magnesium is somewhat doubtful but is disqualified as a deoxidizer from a practical standpoint.

Aluminum, zirconium, titanium, and boron all are capable of producing No. II type sulphides. On a comparison basis, aluminum and zirconium seem to be about equal and are the strongest deoxidizers of the elements tested. Titanium is next, though considerably weaker, while boron is not quite as good as titanium.

Alumina (acid-insoluble aluminum) was found to be quite constant in carbon steel for a wide range of residual aluminum contents. This is explained on the postulate that it was in solution in the molten steel as AlO, which precipitated and disproportionated to $Al_2O_3 + Al$ during freezing.

The theory that deoxidation is primarily a homogeneous reaction involving monoxides of Fe and the deoxidizing element is expounded. Oxides above the solubility limit precipitate and disproportionate to higher valence oxides.

By use of the proper chemical species in deoxidation, equilibrium constants may be obtained which are independent of activity coefficients.

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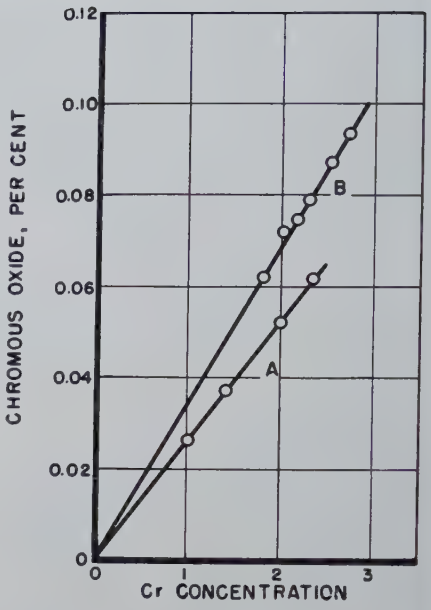

FIG 8—Values of [CrO] from Table 3.

Plotted against the square root of [Cr] contents up to 5.5 pct Cr (curve A) and against the cube root of [Cr] contents from 5.5 to 20.0 pct (curve B).

DISCUSSION

J. CHIPMAN*—This paper describes the use of a new kind of indicator for studying the relative deoxidizing powers of several elements used in the deoxidation of steel. This is a very clever device and the results are interesting and possibly useful. The experimental method deserves careful scrutiny in order that there may be no uncertainty about what the indicator indicates. Molten steel, apparently at 2900–2950°F in a basic-lined induction furnace, is deoxidized first with manganese and silicon and then with small increments of other deoxidizers. After each addition a 3-in. ingot is cast in a sand mold. The shape of the sulphide inclusions therein undergoes a sharp change with a critical amount of each of several deoxidizers and it is assumed that this change corresponds in each case to the same degree of deoxidation of the melt.

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* Massachusetts Institute of Technology.

Two limitations on the use of this indicator must be recognized. The first is that, in order for this indicator to indicate the same degree of deoxidation with different deoxidizing elements, the composition of the indicator must be independent of the kind of deoxidizer used. Our present lack of information on the constitution of sulphide inclusions should caution us not to consider the indicator as an exact criterion of deoxidation but rather as a potentially useful approximation.

The second limitation arises from the fact that the sulphide inclusions are formed during the solidification of the metal, and the indicator can therefore be applied only to the condition of the metal during solidification. This means that its results should be compared not at 1600°C but in the freezing range, which is, of course, the condition of greater practical importance. This is a point which the authors have apparently overlooked and it deserves considerable emphasis. The degree of deoxidation indicated is not that in the furnace but rather that in the ingot during solidification. The amount of deoxidizer which must be added to the melt in the furnace must be large enough to react not only with the oxygen present but also with any additional oxygen which may be absorbed during pouring. If the solubility of the deoxidizer in the melt is very small it may be impossible to add enough of it in the furnace to maintain a high degree of deoxidation in the ingot. The solubilities of both magnesium and calcium in liquid steel are known to be very small and it seems evident that the results reported for these two elements have no bearing whatever upon their deoxidizing power. It is true that ways and means for utilizing the strong deoxidizing powers of these gaseous elements have not been developed, but the only contribution which the authors have made to this problem is another method to be avoided.

The validity of the experimental work on deoxidation with aluminum, like all previous attempts to study this reaction, is heavily dependent upon the accuracy of the analytical methods. When dealing with aluminum contents of the order of 0.006 pct, one must inquire diligently regarding the details of the method as well as possible interferences of such elements as carbon and nitrogen. Moreover, the assumed constancy of insoluble aluminum upon which so much argument is based seems hardly to be supported by the cited work of Wentrup and Hieber. Their acid-insoluble aluminum ranging from 0.001 to 0.012 pct (a twelve-fold range) can scarcely be considered a "significant corroboration" of this supposed constancy.

With regard to the theoretical sections of this paper, perhaps it will be sufficient here to record complete disagreement.

C. E. SIMS (authors' reply)—We concur with Dr. Chipman in pointing out the limitations of the deoxidation indicator used in this study. For example: at best, it is useful to indicate only one degree of deoxidation, that at which Type II sulphides first form. It is also limited to those deoxidizers substantially stronger than silicon; the others are merely lumped in the class of weak deoxidizers.

Its usefulness may be illustrated by the fact that it places vanadium very definitely among the weak deoxidizers, whereas, until recently, it has been widely regarded as a powerful deoxidizer. Statements in reference books and earlier thermodynamic calculations fostered this opinion.

The first limitation set by Chipman does not appear serious. The fact that the change from large globular to fine eutectic sulphides occurs at such low concentrations of deoxidizers, 0.002 pct for Al or Zr, makes it quite unlikely that these elements could materially alter the composition of the sulphides. It is quite obvious, on the other hand, that, at higher concentrations, sulphides of the deoxidizers do form.

In regard to Chipman's second limitation, it is emphasized again that the primary objective was a comparison of deoxidizers. The deoxidation was carried out at a nearly constant temperature of 1600°C. After that, the heats were held a standard time of 45 sec and poured directly into the mold with minimum exposure to air. Obviously, in all experimental work at high temperatures, the specimens must be solidified and cooled before they can be examined or analyzed and some conditions change during that operation. In the present case, the sulphides form during solidification, but it is postulated that the form they take is a direct result of the deoxidation that occurred at the holding temperature of 1600°C. When a different amount of deoxidizer was added, a different result was obtained. Because of the conditions of handling, it is believed that very little change took place in the content of residual deoxidizer during pouring and solidification. This is attested by the constancy of the alumina content.

The difficulties of using such volatile and insoluble elements as calcium and magnesium as deoxidizers for steel were pointed out in the paper. Perhaps they did not have a fair chance to show their powers, although they were used in the customary manner, and perhaps they are strong deoxidizers as Chipman maintains, but what is the evidence? In another test, calcium vapor was bubbled through a rimming-type steel for a protracted period without showing any evidence of deoxidation. Although suitable under strongly oxidizing conditions, magnesia crucibles have been found unsuited to experimental work with steel under reducing conditions because the magnesia was reduced and volatilized. Alumina under the same conditions was quite satisfactory.

It is readily conceded that the present wet methods of determining Al in steel leave something to be desired. The method used is one generally approved by metallurgical laboratories. Carbon and nitrogen apparently do not interfere because the carbides and nitrides of aluminum are readily soluble in acid. The analyses reported by Wentrop and Hieber, taken by themselves, would have no significance. Although they do have considerable scatter, they lend some support to other, more consistent analyses. Because of the analytical difficulties and very low concentration, a "twelvefold" variation is actually not too bad from an analytical standpoint, and, of course, most of the results were much closer to the average value. As pointed out in the paper, even the highest results of 0.012 pct represent only a small fraction of the total aluminum that was oxidized when aluminum was added.

In regard to the theoretical sections of the paper, it was fully anticipated that there would be considerable disagreement, but that alone was not a deterrent. The theory is an attempt to explain observed phenomena not covered by previous theories, but it should not be accepted without critical examination. The alternative seems to be to fall back on assertions that the oxygen content of liquid steel has a low activity because of some vague interatomic attractions and the use of a "fudge factor" called an activity coefficient, when making calculations. The present theory is immature, but, until it is disqualified, it appears to have the advantages of simplicity and workability.

Discussion[*]

Iron and Steel Division

San Francisco Meeting, February 1949

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[*] TP 2712 C.

Tracer Study of Sulphur in the Coke Oven

By S. E. EATON, R. W. HYDE, and B. S. OLD

DISCUSSION

(George McMeans presiding)

G. McMEANS[*]—This paper is a very good demonstration of the use of a new tool for the solution of industrial problems of a physical nature. To have solved this problem without the use of radioactive tracers would have required a far greater amount of investigation and work. The authors have described their work in such detail and in such a manner as to suggest the possibilities of the use of such tracer studies in the solution of many perplexing problems of industry.

R. E. BREWER[†]—The authors are to be congratulated on this very excellent paper, which describes the results obtained by utilizing radioactive tracers in investigating the complicated reactions in the coking process. The paper has especial merit because the study was made under typical operating conditions in a commercial coke oven. Considering all the difficulties involved, the results obtained are excellent. My brief comments will relate primarily to the method used for determining the sulphur in the gas and to the value of the data obtained in stimulating further research.

In discussing their results, the authors state (p. 17) that "Of the total sulphur charged to the oven in the coal 95 pct was accounted for in the coke and gas. Most of the sulphur unaccounted for is believed to have been lost in the gas, since the gas sampling system removed all the H_2S but probably only part of the organic sulphur compounds present in the gas. Although sulphur in the acid-insoluble tar residue in the gas scrubbing bottles was determined and added to the total sulphur determination of each sample, it is doubtful whether an aliquot portion of tar for each sample was obtained." The reviewer believes that the authors might have obtained a better sulphur balance had they used an improved procedure for determining sulphur in the gas.

The absorption train should have included a trap to remove the tar and ammoniacal liquor and a wash bottle containing 5 pct sulphuric acid to remove ammonia in the coke-oven gas before it entered the gas scrubbing bottles containing the ammoniacal cadmium chloride solution. Sulphur in the tar and liquor could then be determined directly; and, at the same time, contamination of the precipitate by tar in the gas scrubbing bottles would be avoided. Ammonia in the gas should be removed to avoid increasing the alkalinity of the ammoniacal cadmium chloride solution, with consequent possible solution of part of the cadmium sulphide precipitate.

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[†] Chemical Engineer, Central Experiment Sta., U. S. Bureau of Mines, Pittsburgh, Pa. Papers by members of staff of U. S. Bureau of Mines are not subject to copyright.

The authors have assumed that all of the dry, purified precipitate is cadmium sulphide from which they have calculated elemental sulphur. In addition to cadmium sulphide formed from the hydrogen sulphide, ammoniacal cadmium chloride solution also precipitates mercaptans as cadmium mercaptides and some of the carbon disulphide after partial hydrolysis as cadmium sulphide. Since the percentages of sulphur in cadmium sulphide and in cadmium mercaptide (ethyl mercaptide) are 22.2 and 27.3, respectively, calculation of the elemental sulphur from cadmium sulphide alone would be in error. Granting that the amount of elemental sulphur might thus be reported somewhat high, the higher value has not compensated for the remaining sulphur in other organic sulphur compounds that may have been present and were not precipitated either as cadmium sulphide or as cadmium mercaptide. The gas-sampling system used must therefore have removed "only part of the organic sulphur compounds present in the gas." However, since the total sulphur present in the organic sulphur compounds—such as mercaptans (ethyl and methyl), thiophene and its homologs, carbon disulphide, carbon oxysulphide, thio ethers, and alkyl disulphides—in coke-oven gas is small as compared to the sulphur in hydrogen sulphide, the total error in assuming that all of the sulphur is precipitated as cadmium sulphide would be small. A more elaborate gas-sampling system using more specific reagents in the absorption train to insure complete removal of all of the sulphur in the gas and additional laboratory analyses to determine the sulphur absorbed by each of the various reagents would, no doubt, afford a better sulphur balance. The additional labor and cost of introducing these refinements, however, to determine the 5.2 pct of unaccounted for total sulphur might not be justified in routine operations.

Fig 8 shows the percentage of sulphur content of coke-oven gas originating from the pyritic sulphur of the coal increases markedly between the 4th and 12th hours of the coking period. On the other hand, Fig 9 shows that the sulphur content of the gas originating from the organic and sulphate sulphur of the coal drops steadily after the 4th hour. These observations emphasize the need for coking coals of low pyritic sulphur content and should stimulate new developments in more effective coal-cleaning methods. Organic sulphur in coal cannot be satisfactorily removed by present methods, but if it is not too large in amount it may be tolerated if the pyritic sulphur is small.

The authors have made a valuable contribution to the knowledge of the coking process. Their paper serves as an excellent guide for determining the principal sources of sulphur in coke. The results of this study should stimulate intensive research in the developments of methods for (1) reducing both inorganic and organic sulphur in the coal charge, (2) converting larger proportions of the coal sulphur into volatile products during coking with resulting lower sulphur in the coke, and (3) treating the coke itself to reduce its sulphur content.

(Attention is called to the following misprints in the text of the paper:

"Ind." in table on p. 4 must mean Allegheny Co., Pa.

"24,198" in line 25, p. 6, should read "24,188."

Sum of values in columns 3 and 4, Table 5, p. 12, for 2d, 5th, and 12th hr do not give the corresponding present values in column 5 of this table. After correction, the sum of all values in column 5 will be 60.5 lb or 24.6 pct of the total sulphur. This slightly higher value for sulphur in the gas, if used, will favor the sulphur balance: Table 6, p. 12; line 1, p. 13; and Table 8, p. 14.).

C. WAGGONER*—The use of a new tool is very enlightening to us who have had mixed feelings toward and recognize the need for collaboration about things like sulphur. I still ask this question. The authors talk about migration and say that it is a reasonable assumption that radioactive pyrites behave identically with the natural pyrites and then in the conclusion the results indicate that there is a migration. I would like to ask is that a migration of sulphur or is it merely a migration of radioactivity?

J. DASHER†—The radioactive sulphur. Sulphur 35 will not make any other sulphur atom radioactive. The element that is radioactive will remain so until it changes into chlorine, so the activity measured in the organic and the calcium sulphide form in the coke shows that the sulphur atoms present in that form in the coke were originally present in the pyrite, and there is no conversion of radioactivity. The atom itself is tagged.

C. WAGGONER—Before we can use a tool we must know a little bit more about it and I was interested in one other part of the paper that dealt with the background of radioactivity. If we are to tag atoms those tagged atoms may cause us trouble later in our product. We can easily calculate at what period of time it would approach the background radioactivity, is that proper?

J. DASHER—Yes.

C. WAGGONER—And are we right in assuming that if we got reasonably close to that there would be no danger from action of radioactivity? I am not thinking about action on the person such as you described—the skin of a person would stop this activity—but I am thinking about, say, photographic plates.

J. DASHER—The activity from the sulphur in this experiment would be insufficient to affect a photographic plate.

C. WAGGONER—Will the detail of the experiment be printed?

J. DASHER—The paper was published. The analytical method in detail will be published.

C. WAGGONER—That will be excellent because I am sure it will answer a lot of questions that we who are confronted with problems of this kind will have to discuss with someone intelligently. I think the authors have made a real contribution to the methods of analyzing steel, and I only wish that we were more able to take advantage of it.

R. W. CAMPBELL*—The authors are to be congratulated on the presentation of an excellent paper and the development of a new and unique method in investigating the complicated reactions in the coking process. The results of this first large scale tracer study stress the value of the use of radioactive isotopes in the study of process metallurgy and will probably stimulate further work where similar approach would be necessary to gain the goal desired.

The rapidity of depletion of low sulphur coking coals and the advent of 100 pct mechanized coal mining in certain mining districts of the United States have given the steel industry a very perplexing problem to solve in order to obtain low sulphur metallurgical coke. The pyritic sulphur, with the exception of the very fine sizes, can be successfully removed in a modern coal washing plant, but the organic sulphur remains untouched, and it is this form of sulphur which the scientists should try to reduce in an economical way.

The Republic Steel Corporation was interested in finding out which one of the two major forms of sulphur in coal, namely, pyritic and organic, contributed the greater portion of the sulphur in the coke. Since, however, considerable quantities of sulphur are present in coke oven gas it was thought that if it could be shown definitely that the major part of the sulphur in coke originates from only one of the major forms of sulphur in the coal it would be possible to select types of coal which, although high in total sulphur, still would yield coke of fairly low sulphur content. This problem seemed to be suited for study using modern radioactive tracer technique while employing full-scale coking conditions, and this certainly has been accomplished by the authors.

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* Superintendent Coke Div., Pittsburgh Dist., Jones & Laughlin Steel Corporation.

The initial radioactive sulphur employed had an activity of only 40 microcuries per g. Due to high dilution factor with inactive sulphur in the coal, the activity was reduced still further and it was found necessary to employ the sulphur present as the pure element in order to obtain sufficient accuracy. Since all samples contained active sulphur of the same age from the original batch, all activity measurements would be directly comparable if they were taken at the same time. As a close approximation, all sulphur samples were counted the same day with frequent checks of the background reading without sample.

The analytical data showed that 70.3 pct of the total sulphur in the coal was retained in the coke, 24.5 pct in the gas and 5.2 pct was unaccounted for. Of the total sulphur in the coal 42 pct was pyritic according to chemical analysis and from the tracer measurements it was found that 40 ± 2 pct of the total sulphur in both the resulting coke and gas evolved had pyritic origin. Thus neither of the two main forms of sulphur in coal, pyritic and organic, is removed preferentially during coking. Employing present coking methods there would be no advantage in choosing coal for its high or low pyritic or organic sulphur content.

Ferrous sulphite and carbon-sulphur complex forms represent all the sulphur in coke under high temperature and reducing conditions, as in the coke oven. After coke is pushed, some of the ferrous sulphite oxidizes to free sulphur and sulphates. However, in the top of the blast furnace, where high temperatures and reducing conditions again prevail, the free sulphur and sulphates revert to the original ferrous sulphite.

The authors conclude that in order to produce low sulphur coke, coals low in initial sulphur must be used and that in view of the large initial evolution of organic sulphur observed in the experiment, coals containing large amounts of organic sulphur and small amounts of pyritic might be coked for a slightly shorter time to produce coke containing a given percentage of sulphur. Coals high in pyritic sulphur would have to be coked for a slightly longer period of time to obtain the same results.

Their conclusions on the possibility of helping the coke sulphur situation by controlling the coking time, depending on the types of sulphur present in the coal charge, is very interesting and should be studied further. It must be remembered, however, that the physical quality of the coke has always been the determining factor governing the coking time.

Without trying to detract in any way from the excellent work done by the au-

Table 9 . . . Distribution of Sulphur in Coal, Coke and Products of Distillation
100 Pct Raw Pittsburgh Seam Coal—Total Sulphur, 1.21 Pct

Forms of Sulphur in Raw Coal

	Pct	Pct of Total
Sulphate sulphur	0.07	5.78
Pyritic sulphur	0.49	40.50
Organic sulphur (humus)	0.52	42.98
Organic sulphur (phenol sol.)	0.13	10.74
Total	1.21	100.00
Inorganic sulphur	0.56	46.28
Organic sulphur	0.65	53.72

↓

Pct Coke Yield	Pct Sulphur in Coal	Pct Sulphur in Coke	Pct Sulphur Eliminated	Pct Sulphur Retained
67.1	1.21	0.94	47.85	52.15

Sulphur in furnace coke	0.94 pct
Sulphur in coke breeze	1.27 pct
Sulphur in gas after saturators	570 grains per 100 cf
Sulphur in gas after final coolers	550 grains per 100 cf
Sulphur in tar	0.69 pct
Total sulphur in light oil	1.02 pct
Total sulphur in liquor	1.495 g per liter
Sulphur as sulphides in liquor	0.520 g per liter

Distribution of Sulphur of Coal in Products of Distillation

	Pct	Pct of Total
In coke	0.631	52.15
In breeze	0.104	8.60
Total in gas	0.387	31.98
In tar	0.031	2.56
In light oil	0.016	1.32
In final cooler water	0.014	1.16
In liquor as sulphide	0.004	0.33
In liquor as ammonium Thiosulphate, sulphocyanate	0.008	0.66
Total determined	1.195	98.76
Undetermined and loss	0.015	1.24
Total	1.210	100.00

↓

	Pct Retained	Accum. Pct
In coke	52.15	52.15
In breeze	8.60	60.75
In gas	31.98	92.73
In tar	2.56	95.29
In light oil	1.32	96.61
In final cooler water and liquor	2.15	98.76
Undetermined and loss	1.24	100.00

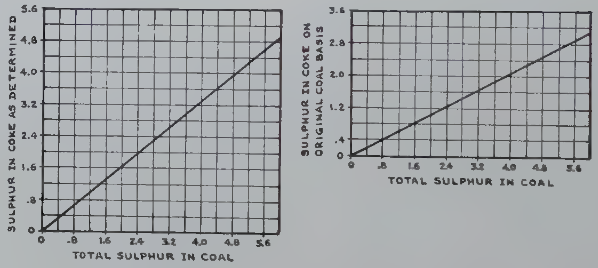

FIG 13—Coal and coke sulphur relationships.

A (*left*)—Relation of sulphur content of coke to sulphur content of coal.

B (*right*)—Sulphur content of coke, expressed on basis of original coal, as function of total sulphur content of coal.

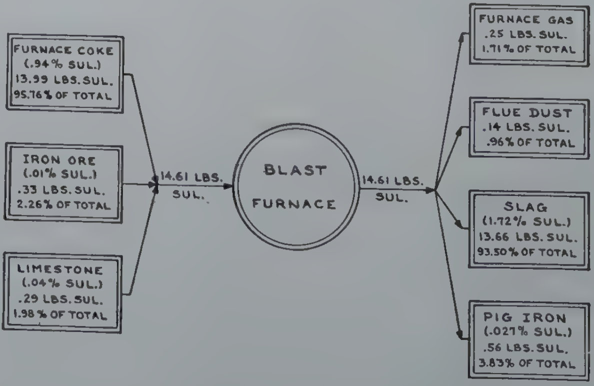

FIG 14—Sulphur distribution in the blast furnace per net ton of pig iron.

thors in their elaborate and excellent study of sulphur, it is interesting to quote the conclusions of two earlier experimenters in the same field:

Dr. A. R. Powell (1920)[14]—"The total sulphur of the coal is the most important factor affecting the sulphur content of the coke and the relative amount of sulphur forms does not affect it materially. Certain other factors, particularly the nature of the coal, vary the amount of sulphur in the coke to a limited extent."

Gilbert Thiessen (1935)[15]—"The sulphur in coke is derived from both organic and pyritic sulphur in the coal, approximately 45 pct of the organic sulphur and 60 pct of the pyritic sulphur remain in the coke.

"Because the proportions of the organic and the pyritic sulphur which remain in the coke are of the same magnitude, the sulphur content of the coke is for practical purposes directly proportional to the total sulphur content of the coal. Approximately half of the sulphur in the coal remains in the coke. Because of the loss of volatile matter, the amount of sulphur in the coke is about 80 pct of the percentage of the sulphur in the coal from which the coke was made. Iron compounds other than pyrites in the coal, arising from infiltration or from oxidation of pyrites, increase the retention of sulphur in the coke."

Fig 13 presents two curves from the experimental work of Gilbert Thiessen and shows; "A—Relation of Sulphur Content of Coke to Sulphur Content of Coal" and "B—Sulphur Content of Coke, Expressed on Basis of Original Coal, as Function of Total Sulphur Content of Coal."

Table 9 is a tabulation of some of the experimental work done at our Pittsburgh By-Product Coke Plant.

Fig 14 clearly indicates that 95.76 pct of the total sulphur in the burden is contributed by the coke containing 0.94 pct sulphur.

E. J. GARDNER*—The authors are to be commended for their careful preparation of an interesting and informative paper on the use of radioactive tracers to determine the distribution of the pyritic and organic sulphur in the carbonization of coal for the production of high temperature coke.

The gas evaluation curves, sulphur balance data on the plant scale test run, and the schematic flow of sulphur in a coke oven diagram, wherein the course of the pyritic sulphur is traced in order to determine quantitatively the amount evolved in the gas and the amount remaining in the coke, form an important contribution to our knowledge of the behavior of sulphur in the coking process.

Table 10—Inland Steel Co. Coal and Coke Analyses and Yields

	June 1941				Dec. 1948			
	Pct in Mix	Pct Ash	Pct Sulph	Pct Yield	Pct in Mix	Pct Ash	Pct Sulph	Pct Yield
Pocahontas	35	5.70	0.60		35	8.05	0.62	
Wheelwright Slack	40	4.05	0.74		45	9.00	0.96	
Wheelwright Egg	25	2.00	0.66		20	4.10	0.80	
Mixture		4.00	0.67			7.40	0.83	
Furnace Coke		5.35	0.58	68.8		10.20	0.70	68.1
Domestic		5.50	0.57	2.3		9 75	0.69	1.9
Braize		9.00	0.61	2.7		15.40	0.76	4.0

Percent sulphur reduction during the carbonization of coal for the production of coke.

	1941	1948
	Pct Sulph. Yield	Sulph. Yield
Furnace coke	$0.58 \times 0.688 = 0.399$	$0.70 \times 0.681 = 0.477$
Domestic	$0.57 \times 0.023 = 0.013$	$0.69 \times 0.019 = 0.013$
Braize	$0.61 \times 0.027 = \underline{0.016}$	$0.76 \times 0.040 = \underline{0.030}$
	0.428	0.520
	$\frac{0.428}{0.67} \times 100 = \underline{63.9}$ pct sulphur left in coke	$\frac{0.52}{0.83} \times 100 = \underline{62.6}$ pct sulphur left in coke

At the Inland Steel Co., we also are concerned at the decrease in the quality of our high volatile—Elkhorn Seam—slack coal as regards ash and sulphur content. When our Wheelwright mine, because of the demand for increased production for the war emergency, went from the customary practice of careful preparation of the coal at the face, followed by hand loading of the coal into the mine cars, to the present practice of machine loading, the ash and sulphur content increased from 4.05 and 0.74 pct in June, 1941, to 9.00 and 0.96 pct respectively in Dec., 1948.

The increase in ash and sulphur in our coal blend produced furnace coke with inferior chemical and physical properties and resulted in a decrease in the quality and the iron tonnage obtained from our blast furnaces.

In order to overcome the adverse effects of mechanical loading on the ash and sulphur content of our high volatile coal, we are installing a coal cleaning plant at our Wheelwright mine. Our mining department assures us that they will deliver washed Wheelwright coal from machine loaded mining with ash and sulphur contents that are similar to the hand loaded product.

Table 10 shows comparative coal and coke analyses for our hand loaded and machine loaded coal.

Table 10 shows that in 1941 our coal mixture had 4.00 pct ash and 0.67 pct sulphur. In 1948, the coal mixture shows 7.40 pct ash and 0.83 pct sulphur. For the same periods, the analyses of our furnace coke went from 5.35 pct ash and 0.58 pct sulphur to 10.20 pct ash and 0.70 pct sulphur.

From the total sulphur analyses of the coal mixture charged and the coke produced, the amount of sulphur remaining in the coke was 63.9 pct for the 1941 and 62.7 pct for the 1948 period; in other words, the percent of the sulphur volatilized in the coking operation was practically the same for the low and high sulphur coal mixtures.

The results reported in the plant scale tracer study have given us a clearer picture than using the conventional methods of chemical analysis, of the rate of evolution and distribution of the pyritic and organic sulphur compounds during the carbonization of coal.

Although it will still be necessary to carbonize coals with low total sulphur content in order to produce low sulphur coke, the experimental data presented by the authors will form the basis for further radioactive tracer studies of the reactions that take place in the course of the transformation of coal to coke.

S. E. EATON, R. W. HYDE, and B. S. OLD (authors' reply)—The authors wish to thank R. W. Cambell and E. J. Gardner for their very interesting comments on the subject of sulphur in the coke oven and the blast furnace, and Ralph E. Brewer of U. S. Bureau of Mines for his very careful review of the paper.

In regard to the 5.2 pct of the total sulphur unaccounted for in coke and gas, Mr. Brewer is correct in saying that more of the sulphur in the coke oven gas could probably have been recovered by an improved scrubbing method. However, we wish to point out that since 95 pct of the sulphur in coke oven gas is present as hydrogen sulphide, the amount of sulphur in the gas which was not recoverable by the system used is rather small. We agree that a slight error may have been introduced by the presence of cadmium mercaptide in the cadmium sulphide precipitate but since sulphur as mercaptans is only on the order 0.3 pct of the total sulphur in the gas the error should be extremely small. Undoubtedly some of the sulphur in the gas passed through the scrubbing train; to have removed all the sulphur in the gas as well as obtain an aliquot portion of tar would have involved a much more elaborate sampling system. Since we were primarily interested in the distribution of the forms of sulphur in the coke, a more elaborate system of sampling gas did not seem justified in view of the probable error involved.

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[14] A. R. Powell: *Jnl. Ind. Eng. Chem.* (1920) 12, 1069.

[15] Gilbert Thiessen: *Jnl. Ind. Eng. Chem.* (1935) 27, 473.

* Superintendent, Blast Furnace and Coke Dept., Inland Steel Co., East Chicago, Ind.

Mr. Brewer also noticed a slight discrepancy in Table 5 for the 2nd, 5th, and 12 hr. The values of pyritic, organic, and total sulphur evolved each hour were calculated to one significant figure to the right of the decimal point, that is, to the nearest tenth of a pound. We would prefer not to change any value in this table as the individual values are more accurate as they now stand.

Some Correlations between Variables Affecting Sulphur in Blast Furnace Iron

By T. E. BROWER and B. M. LARSEN

DISCUSSION

(G. MacMeans presiding)

J. SAUSSAMAN*—One thing I have to say is that when anyone mentions sulphur, we at Fontana, are ready to listen. Although we do not have too much sulphur in our coke, we run into sulphur in our ores, and that is just one more variable in the question of how to control sulphur. Inasmuch as most of the data for this paper were taken from actual operation, I thought it might be interesting to show you some places in our operation which vary from those covered in the paper. The authors talk quite a bit about magnesia in the slag, and the magnesia in the slag at Fontana runs anywhere from 15 to 18 pct, usually being closer to 18 than 15. We get very good sulphur elimination with this slag, although the calcium in the slag is very much on the low side—about 32 pct. The high magnesia content does not appear to affect seriously sulphur elimination.

At the present time the two ores we use carry quite a bit of sulphur, one of them 2 pct sulphur and the other about 0.5 pct sulphur. Of course, the 2 pct sulphur ore cannot be used in the furnace directly due to that amount of sulphur, but it is removed by sintering. That reminds me of the statement that was made in a recent paper that the best way to control sulphur is not to put it in in the first place, so that is the way we do with the ore and have very good results with the sintered product.

The other ore contains about 0.5 pct sulphur and we control the sulphur merely by a screening operation which reduces the sulphur to about 0.2 pct in the plus ⅝ in. particles with a large percentage of the sulphur following the minus ⅝ in. particles to the sintering plant.

In this one ore, running about 0.5 pct sulphur, we have the problem that half of that sulphur is in the form of gypsum or calcium sulphate, and the question then comes up as to how to control sulphur when it is in the form of calcium sulphate. Does it react in the same way in the furnace as the pyritic sulphur? We do not know the answers as we have not been working with it long enough.

L. E. RIDDLE*—I do not think it right to state that some one thing is the reason sulphur in pig iron is high or low. You have to take into account a number of things—variable amounts of sulphur when using the same materials, the kinds of sulphur in the raw materials, temperature changes in the hearth of the furnace, and correlation effect.

I do not agree with Mr. Larsen that varying amounts of alumina has no effect on slag. His data show that in his study of more than 100 samples of slag the alumina did not vary 1 pct. Had he had slags with Al_2O_3 as low as 9 pct and others with 20 pct he would have found that with Al_2O_3 above 18 pct the ratio of CaO and MgO to $SiO_2 + Al_2O_3$ can be lowered greatly with sulphur removal, results equaling those when the CaO and MgO ratio to $SiO_2 + Al_2O_3$ is much higher when the Al_2O_3 is below 15 pct.

Having made pig iron with 19 and 20 pct Al_2O_3 in the slag and ferro-manganese with 22–23 pct Al_2O_3 and the same products with half these amounts of Al_2O_3 in the slag, we learned the above fact.

B. M. LARSEN (authors' reply)—Mr. Saussaman's comments indicate approximately normal or expected S removal at 15–18 pct MgO in slag with 32 pct CaO. We have experience in one shop with 10–12 MgO and a limited run in another with 15–17 pct MgO; in both cases the ratios were lower by only a moderate amount than at what we feel to be the optimum range of 6–8 pct MgO. All such comparisons between shops must be regarded with caution because of the many factors (manganese and silicon in iron, iron and slag temperature, etc.) which appear to complicate the sulphur removal situation. As regards the division between pyritic and sulphate sulphur, we believe that essentially all the sulphur charged gets trapped in the furnace and all of it ends up in the sulphide form, so it does not matter in what form it is present in the charged materials.

As regards a member's comments on the factors of Mn and temperature, we would only say that until a lot of good temperature data are available on slag and metal casts, we probably must keep an open mind on the interrelationships between different variables. Higher temperature may have a direct effect of speeding the rate of sulphur migration from iron to slag. On the other hand, to the extent that higher temperatures are associated with higher Mn and Si and more basic slags it is quite probable that here the temperature should be regarded as the secondary rather than the primary variable.

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Sulphur Equilibria between Iron Blast Furnace Slags and Metal

By G. G. HATCH and J. CHIPMAN

DISCUSSION

(G. MacMeans presiding)

T. ROSENQVIST*—It is a pleasure to see the excellent way in which the experimental part of this work has been handled. There seems to be little doubt that the distribution data obtained corresponds most closely to thermodynamic equilibrium under the prevailing reducing conditions, namely equilibrium with graphite and one atmosphere CO pressure.

The desulphurization curves in Fig 10 show the same general feature as the curves given by Holbrook and Joseph, but the distribution ratios are from 20 to 40 times greater—undoubtedly due to a closer approach to true equilibrium.

In the theoretical discussion, the authors calculate a theoretical distribution ration $\frac{(S)}{[S]}$ which they find to be about 50 times greater than the experimental. The deviation is so great that the basis for their calculation needs a more thorough examination.

The authors base their thermodynamic calculation on free energy expressions where diluted solutions of FeS and CaS are used as standard states. (The activity coefficient in diluted solutions is taken to equal unity.) Such a standard state will change when the nature of the solvent is changed. Taking the free energy of the reaction $[FeS] \rightarrow (FeS)$, Eq 2, which is derived from the distribution of sulphur between an iron and a FeO-melt, it is very unlikely that the free energy of this reaction will be the same for a distribution between pig iron and a calcium silicate slag.

Therefore a more fundamental basis for the thermodynamic calculations seems needed, where all thermodynamic equations are referred to unambiguously defined standard states.

The most natural standard states for CaO and CaS are the pure solid substances at the same temperature. As standard state for sulphur in iron, pure liquid FeS can be used. This rules out Eq 2 $[FeS] \rightleftharpoons (FeS)$ because $\Delta F^\circ = 0$. The standard equation will then be:

$$FeS_l + CaO_s + C_{graph} \rightarrow Fe_l + CaS_s + CO_g$$

$$\Delta F^\circ_{1773} \approx 25{,}000 \text{ cal}$$

It would be more universal and also simpler to refer the escaping tendency of sulphur in liquid iron to the corresponding H_2S/H_2 ratio which can readily be determined experimentally. As standard state a gas mixture $H_2S/H_2 = 1/1$ can be used. (This corresponds at the temperature of liquid iron closely to one atmosphere S_2 vapor.) Thus the standard equation for the sulphur reaction can be formulated as follows:

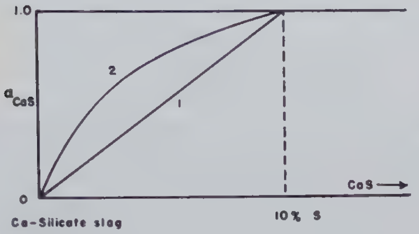

FIG 11—Chemical activity of CaS in blast furnace slag.

(Hypothetical) Curve 1. Approximately ideal solution. Curve 2. Positive deviation from ideal solution.

$$H_2S_g + CaO_s + C_{graph} \rightarrow H_{2g} + CaS_s + CO_g$$

The standard free energy of this reaction has been calculated from the best available data to $\Delta F^\circ_{1773} = -35{,}000$ cal. This gives for the equilibrium constant at 1500°C

$$Kp = \frac{A_{CaS} P_{H_2} \cdot P_{CO}}{A_{CaO} \cdot P_{H_2S} \cdot A_C} = 2.10^4$$

Now, the solubility of CaS in blast furnace slags has been determined by McCafferey and Oesterle* and corresponds at 1500°C to about 10 pct S (varying somewhat with the composition of the slag.)

If the activity of CaS is assumed linear between 0–10 pct as curve 1, (see Fig 11), then $a_{CaO} = 0.1$ (S); (S) being wt. pct sulphur in the slag.

For a diluted solution of sulphur in an iron melt saturated with carbon, the ratio H_2S/H_2 is, according to Kitchener, Bockris and Liberman,† about 0.01 [S], [S] being wt. pct sulphur in iron. Substituting these values in the expression for K_p we find

$$\frac{(S)}{[S]} = 2.10^3 \cdot a_{CaO}$$

The value 2.10^3 is only 4 times greater than the experimental coefficient found by Hatch and Chipman, but the value is very sensitive to a small error in ΔF°.

A better agreement with the experimental distribution coefficient can be obtained if one assumes the activity of CaS to run like curve 2 (Fig 11). This will give a lower theoretical $\frac{(S)}{[S]}$ value, a value which varies with (S) exactly as Hatch and Chipman learned. Such a shape of the activity curve, which corresponds to a positive deviation from Raoult's law, is actually to be expected from the fact that liquid silicate and sulphide phases usually show incomplete miscibility.

A closer agreement between experimental and theoretical data can not be expected before we have more complete data for the individual activities of CaS and CaO in the slag. The activities a_{CaS} and a_{CaO} referred to the solid phases as standard states, are exact defined quantities contrary to the somewhat undefined expression "free lime," and they are independent of any theory for the constitution of liquid slag.

J. CHIPMAN (authors' reply)—The authors wish to thank Mr. Rosenqvist for his very interesting and useful thermodynamic addition. Curve 2 of his figure offers the needed basis for explaining the increase in the ratio (S)/[S] with increasing sulphur content. Attention is called to an error in the printed paper: Fig 2 and 3 are reversed.

M. TENENBAUM*—In the figures showing the relationship between excess base and sulphur distribution (Fig 6, 7 and 9) the slope of the curve tapers off in the negative basicity range. Somewhat the same thing is observed with open hearth slags. In that case, the fact that some sulphur distribution between slag and metal is obtained with negative basicity is interpreted as indicating some dissociation of the lime silicate compounds whose existence in oxidizing basic slags has been used to explain various observed phenomena with regard to other slag-metal reactions. In the case of the blast furnace slags, the reduced slope of the sulphur distribution curve with decreasing excess base is attributed to the amphoteric effect of alumina. Has the possibility of other explanations been investigated?

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* Inst. for the Study of Metals, Univ. of Chicago.

* Trans. AIME (1923) 69, 606-634.

† Discussions of The Faraday Society (1948) 4, 49.

* Inland Steel Co., East Chicago, Ind.

B. M. LARSEN*—In view of this effect of alumina that we failed to find so far in most plant practices, if I interpret that triangular diagram correctly, it seems to me that the lines indicated very little effect of alumina and there was not any effect on sulphur at all.

I am not accustomed to using the triangular diagram, but you will notice these lines fall almost parallel to those corners (*Indicating slide*). That would indicate the alumina has a quite small effect which would agree with what our experience has been in most plant data.

There was one other thing—this departure from the distribution laws would be a very nice thing if it really worked out in practice because we are getting into higher sulphur content in the slag all the time. I am a little skeptical about it. I feel more work should be done, probably more work with higher sulphur contents in the metal phase to minimize analytical errors. In other words, it looks as though this point is so important as to deserve more exhaustive equilibrium studies to make more sure of this effect because it would be desirable to be able to increase the sulphur in the slag.

J. CHIPMAN—We agree with you that more work needs to be done with higher precision on the sulphur analysis. These sulphur analyses were made with extreme care and the method was checked repeatedly against standards. The sulphur analysis was done by the combustion method in a manner which is perhaps better than one would normally encounter and results were always duplicable within ±0.001 pct. Had we known that these sulphurs were going to come so low I think we would have started out in the first place to use radio isotope methods for improving the precision of the analyses. We expected to get sulphur distribution ratios more or less in the neighborhood of what is found in the blast furnace. Even with 5 pct sulphur in the slag we were still able to get unexpectedly low sulphur contents in the metal. There is no doubt about the result that we have shown—that if you double the sulphur content of the slag you do not double the sulphur content of the metal in equilibrium. The ratio (S)/[S] is not a constant.

With regard to the effect of alumina, the results show clearly that it behaves as an acidic constituent in the basic slags. In the more acid slags this characteristic seems less pronounced. No detailed explanation of this observation is required.

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Relation between Chromium and Carbon in Chromium Steel Refining

By D. C. HILTY

DISCUSSION

(*B. G. Emmett presiding*)

C. E. SIMS*—This is a most interesting and important paper. It is important from two standpoints. First, it has aspects of being highly accurate and therefore extremely useful to the operating man in showing how far he can go in oxidizing carbon from a steel bath while retaining chromium and the effect of temperature on this limit. Fig 5 is undoubtedly the highlight of the paper, and in checking it against available data, it seems capable of predicting actual results.

The other important aspect is the apparently significant fact that reactions within a steel bath, such as between carbon and an oxide, are homogeneous reactions which do not require equilibrium with an external phase. In this case, it seems obvious that the reaction and the equilibrium established were between dissolved carbon (or carbide) and dissolved CrO. The classic reaction which requires equilibrium with solid Cr_2O_3 did not fit the data. It was recognition of this principle that made Fig 5 possible.

G. R. FITTERER*—It might be in assuming the CrO is dissolved in the metal that you are actually approaching the correct factor for activity. If that is true and if the percentages that were used represent an equilibrium constant, this would mean, in effect, that the minimum temperature at which chromium would be reduced by an equivalent percentage of carbon would be about 2400°F from your equation. I believe that is in line with my experience particularly if you deal only with low percentages.

J. CHIPMAN†—The author in discussing the equilibrium of the reaction offers two choices of explanation. One postulates an effect of chromium on the activity coefficient of carbon; it would require perhaps more data than are available to us at the present time to test this thoroughly. The other postulate which he offers is a reaction with CrO. This explanation is consistent with physical and chemical principles provided that a solid phase CrO is present, and that is essentially what he is postulating. If that oxide were present one would expect and, I think, almost require the kind of results that he obtained. The weakness of that postulate lies in the lack of confirmatory evidence regarding the presence of solid CrO as such. This should offer an interesting subject for further study.

It seems a pity that the theoretical arguments revolving around CrO should have obscured for a moment the very real excellence of this paper.

E. CARTER*—I think there is a problem that presents itself in practical application where the metal temperature is from 3200 to 3300 and the temperature desired in pouring is considerably less.

B. M. LARSEN†—I get the impression from some of the work that was done earlier that there is probably a localized zone of high temperature at the slag metal interface which effects the removal of the carbon. Without that I wonder if the effect is possible to have a localized superheat and an equilibrium there favorable to low carbon content and still not have the whole bath heated up to that equivalent temperature.

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[*] Univ. of Pittsburgh, Pa.
[†] Professor of Metallurgy, Mass. Inst. of Technology.

[*] Vulcan Steel Foundry.
[†] U. S. Steel Corporation.

D. REEDER*(replying for author)—I do not doubt there is a localized area there, but still the agitation of the bath, particularly at these temperatures, and the effect of applying the oxygen, (blowing the oxygen in there) will give a stirring effect; and also the temperature is so great the molten metal is very liquid and would tend to circulate more.

B. M. LARSEN—In practice you have a heavy liquid below. That heavy liquid may not get stirred very deeply.

D. REEDER—That is true. This is under very high oxidizing conditions and I believe that would have an effect on moving the metal itself.

B. G. EMMETT—I might say along those lines that our experience has been in the injection of oxygen in an arc furnace you get a violent action which would, I believe, tend to stir the metal. I would also like to comment along the lines of this paper. It has been my experience—belief at any rate—that there has been positively too much chromium steel made with no effort to boil. Consequently, when you machine the castings you find them full of holes. If you give the metal a good boil it tends to liberate hydrogen and make a good clean piece of steel rather than one that is full of gas.

D. C. HILTY (author's reply)—It is gratifying that the results presented in the paper seem to be consistent with Dr. Fitterer's experience. Mr. Larsen has brought up an interesting point for speculation. I am inclined to agree with Mr. Reeder and Mr. Emmett, however, that the rather considerable bath action that results from oxygen injection goes a long way toward equalizing temperature throughout a steel bath except, possibly, in a very localized zone immediately adjacent to the point of oxygen input.

With regard to the CrO postulate and the interpretations placed upon it by Mr. Sims and Dr. Fitterer, I believe my position has been adequately stated by Professor Chipman. As pointed out in the paper, the metallic phase was assumed to be in contact with a nonmetallic phase saturated with CrO at steelmaking temperatures. In this connection it is notable that slag samples taken from chromium steel heats at the end of the oxygen blow have been observed to contain particles of metallic chromium as well as chromic oxide and chromite. One possible explanation for these observations is that at high temperatures the slags may have contained CrO which decomposed on cooling in a manner analogous to the decomposition of FeO.

The primary objective of this investigation was to establish an empirical relation that would be of practical value to the operator in establishing a practice for melting chromium steels from charges containing chromium. The chromium-carbon-temperature relation shown in Fig 5 of the paper has been checked in the field in both basic and acid arc furnaces and has been found to hold quite well under both conditions. In a number of instances practices have been deliberately devised on the basis of the curves of Fig 5, and in all cases the heats behaved in the furnace as predicted. It would appear, therefore, that regardless of the theoretical explanation of the results presented in the paper, the primary objective has been attained.

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* Los Angeles Steel Casting Co.

The Effect of Hydrogen on the Ductility of Cast Steels

By CLARENCE E. SIMS, GEORGE A. MOORE, and DONALD W. WILLIAMS

DISCUSSION

(R. C. Madden presiding)

G. A. LILLIEQVIST*—I wish to compliment the authors on the excellent manner in which they have presented their data. The improvement of ductility obtained on test bars after aging at room temperature or at low temperatures of around 400°F has been a well-known fact for many years. The authors have found an explanation for this phenomenon and have presented in their paper conclusive proof that hydrogen plays an important part in controlling ductility values.

While we have never attempted to analyze for hydrogen, a great deal of our time has been devoted to the study of aging treatments to improve the ductility of steels and we have found results similar to those presented in this paper. It was our finding that in practically 100 pct of the steels investigated there was a definite improvement when 1-in. bars were aged at 400°F for 16 hr, 550°F for 1 hr or at room temperature for 4 months. We also noted that the heavier sections were more affected than light sections and that more time was required in the aging treatment to obtain the maximum ductility.

In our investigation we also noted when an acid electric furnace heat was made as rapidly as possible, that is, to obtain a vigorous boil to reduce the carbon and then tapping as soon as possible, good results were obtained. Very little improvement was obtained in aged bars over unaged bars. They were both very good.

I again wish to state that the authors have done an excellent job in presenting interesting information regarding the causes of low ductility values in unaged bars which should be of considerable benefit to the steel casting industry.

C. E. SIMS (authors' reply)—The authors appreciate the comments of Dr. Lillieqvist which give confirmation from practice of the data presented. The work of many investigators, including Dr. Lillieqvist, has tended to establish beyond doubt the effect of hydrogen on the ductility of steel, but this has been largely of a qualitative nature. The present work was designed to test and substantiate these observations and put them on a quantitative basis.

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The Origin of Silicate Inclusions in Basic Electric-arc-furnace Steel of Higher Carbon Contents

By AXEL HULTGREN

DISCUSSION

(*R. C. Madden presiding*)

G. R. FITTERER*—In discussing this paper I would like to state simply, that Professor Hultgren's objection to Stokes' law is interesting but not necessarily a correct interpretation. I would like to point out that Stokes' law states that the velocity of a particle, either when precipitated or rising in a fluid, is dependent chiefly upon three factors. One of these is the viscosity of the fluid which in this case is liquid steel. Another is a difference in density between the liquid steel and the nonmetallic inclusion and the third is the square of the radius of the inclusion particle itself. Now, if the particle has a radius in one case of ten times another, the one with the larger radius will be eliminated at one hundred times the velocity. This law states, in effect, that rain drops cannot become as large as watermelons and it is very fortunate that they cannot.

I would also like to point out that since it is a limiting law, it indicates that it might control either the agglomeration of the silicate particles or their dispersion. In other words, a particle may coagulate with others until the limiting size is reached. Any growth beyond this will cause the large particle to break up into smaller ones other conditions being the same. On the other hand, if in the action of pouring the heat considerable turbulence is present in pouring into the mold or even tapping in the ladle the limiting velocity as demanded by this law might be exceeded and therefore cause the break-down of the inclusions into the form that we saw here. Now, whether or not the small particles that are broken off from the large inclusions as shown, redissolve in the steel is a point which is disputable and has not been proved by this paper.

B. M. LARSEN*—We have a few samples taken from open-hearth furnaces. I do not know whether they illuminate this question, but we took samples from the tapping stream and also out of the ladle. They came out very logically, looking at it from Hultgren's viewpoint. The tapping stream samples from open-tap heats with no block in the furnace had no inclusions except extremely tiny ones. In the ladle the inclusions jumped up to a volume percentage about the same as Hultgren found though of considerably smaller average size. The larger ones were gone in the platform samples.

A. HULTGREN (author's reply)—I wish to thank Dr. Fitterer for kindly taking the trouble to present my paper. To his comments regarding Stokes' law and its application to the present problem my reply is that I am not aware of having objected to this law, in thought or writing. If inclusions, by growth or coagulation, reach a certain size they will rise at a considerable velocity and collect at the top surface of the liquid steel. The results of experiments with steel held in the ladle for different periods, as shown in Tables 5, 10 and 13, agree well with Stokes' law.

The breaking down of large slag inclusions—or rain drops—into small ones as caused by turbulence is not demanded or governed by Stokes' law which applies to conditions of nonturbulence.

Dr. Fitterer apparently interprets Fig 10–14 as evidence of large inclusions breaking down owing to turbulence in pouring. I think, on the other hand, that those figures support the idea of reaction products forming temporarily around inclusions which are not in equilibrium with the metal. My arguments are:

1. The inclusions had no doubt been deformed from turbulence during pouring but their round or rounded shape indicates that the turbulence had largely subsided when they were caught by the freezing steel.
2. If the satellites were formed by fragmentation of the large inclusions in connection with deformation they would not be likely to remain in a surrounding zone of uniform thickness after the latter assumed its rounded shape. Fig 15, on the other hand, shows small inclusions irregularly dispersed in relation to a large one, possibly as a result of fragmentation.
3. The lack of equilibrium at the time of formation of the inclusions is evidenced by the change in appearance of the inclusions while the steel is held in the ladle (Tables 5 and 14), the change observed indicating that the metallic oxide contents are gradually decreasing.

The absence of satellite zones around the inclusions in the samples taken from the ladle are evidence of their short-lived existence. The dissolution of small particles during the simultaneous growth of larger ones in the same matrix is a common occurrence in metallic systems. The low oxygen content of the metal would also favor dissolution. As Dr. Fitterer says, however, this is a disputable point.

The results reported by Mr. Larsen from his study of open-hearth steel supply valuable additional evidence. In conclusion, I ought, perhaps, to emphasize the limitation indicated by the title of the paper: the conclusions drawn are not necessarily all applicable to low-carbon steels.

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Sintering Characteristics of Minus Sixty-five and Twenty Mesh Magnetite

By A. STANLEY and J. C. MEAD

DISCUSSION

(*E. H. Rose presiding*)

E. H. ROSE*—You have wrapped up a great deal of new and interesting information in one quite compact package, and I wonder if it might not help the audience a bit if you would just recapitulate your main conclusions—not all of them, but the outstanding ones about the size, the reactions, and so forth.

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* Tennessee Coal, Iron and Railroad Co., Birmingham, Ala.

J. C. MEAD (authors' reply)—In our research work, the following factors were found to have a very pronounced effect on the minus sixty-five mesh magnetite.

The use of 20 to 30 pct of sized return fines in the prepared feed, when using a hearth layer over the grate area, was very beneficial. Before the sized returns were investigated, and the amount controlled, the results of the tests varied widely due to the fluctuating amount of dust in the "returns."

The control and stabilization of the moisture percentage in the magnetite and coal culm permitted more efficient mixing of these materials which raised the production rate and decreased the amount of coal culm required.

Close moisture control in the prepared feed is essential when sintering at a vacuum of 40 to 50 inches water gauge. Either too high or too low a moisture control will permit the bed to "pull holes," short-circuiting the air and decreasing the production rate.

Accurate control on the amount of sinter fuel in the prepared feed increases the quality and quantity of sinter produced. An excess amount of coal caused too high a fusion temperature which slags and makes a very brittle sinter. Too little coal resulted in too low a fusion temperature which made a weak sinter containing some unsintered material.

While the research work in the test pan showed that minus twenty mesh magnetite can be sintered without much control, in actual plant practice, very close control is needed on the magnetite, coal, and prepared feed. The plant will maintain a high production rate if the moisture in the prepared feed stays between 5.5 to 6.0 pct. Any variation above or below this range lowers the plant production rate.

A variation of 3/10 pct of anthracite coal in the prepared feed will change the production rate.

Any fluctuations of "dust" from the return fines and from the dust collectors can cause wide variations in the moisture of the prepared feed. If the "dust" is used at a uniform rate, it simplifies moisture control and does not affect production.

The use of return fines having a maximum particle size of minus ⅜ in. in the prepared feed and the use of a thick hearth layer over the grate area have been tried on the 250-sq ft pans and have increased the production rate. However, the use of smaller return fines requires closer moisture control than before because the bed does not hold together during the sintering quite as well as it did when using the coarse return fines in the prepared feed.

In all cases in research and in operation the closer the control maintained over the magnetite, coal, return fines, dust, and moisture, the higher were the quality and quantity of sinter produced.

E. H. ROSE—The presentation that Mr. Mead has made here today is one of acute interest to practically all iron ore producers, particularly in view of the fact that we are going to be faced with some very finely divided material when we proceed further with low grade iron ores.

G. J. HOLT[*]—I missed the first part of the paper, but I heard Mr. Mead talk about pellets. I did not get the significance of the pellets.

J. C. MEAD—This pellet we found was due to fine magnetite building up around return fines, and in our test we added water into our returns in the latter part of the mixing to eliminate them. During the first part of our tests we put the water right in with the magnetite, mixing it with a concrete mixer, and we found that in going over the lifters it was rolled up into a ball. Contrary to our original idea that pellets would help us, we found that after the sintering we could take these particles and crush them with our fingers; they break up eventually; they also formed zones of weakness where in being dropped or given a tumbling test they broke down the quality of our sinter.

F. D. DE VANEY[†]—I just wanted to make this comment on the magnetite we are going to pelletize this year. It is about 1 pct on a hundred mesh and about 85 pct minus 200 mesh. We have recently carried on some tests using Dwight Lloyd machines and we found that for this fine material we can get a fair capacity and make a nice sinter if we roll our concentrates into balls that are from ⅛ in. up to approximately ½ in. in diam. We found with such material, contrary to pelletizing, that the added coal had to be placed on the outside of the pellets. In other words, we rolled these balls up in a drum and then we introduced this coal about a foot or two from the discharge end of the drum and put a layer of coal around the pellets; then we put them on the sintering pan and in that way we made a rather nice sintering on the Dwight Lloyd machine. Do you plan on making your pellets in a rotary drum?

MEMBER—We have not had a lot of experience, just 6 months or so on the rolling pellet, and I do not want to get into too much of a discussion on that; but we proposed using the same methods and the size of the balls is directly determined by the percentage of moisture in the balls. If you keep that moisture down the balls will get no bigger.

A. C. RICHARDSON[‡]—As I listened to this paper, I found it a little hard to follow some of the conclusions reached from the data which are worthy of serious study. We have had some experience, in the laboratory, in sintering various types of ores and find that there is very little information of value in literature on this subject. I hesitate to talk about sintering in the presence of Mr. Holt, Mr. DeVaney, and Mr. Johnson who have had a lot of experience with this subject, but a lot of the sintering practice, as far as I can see, is fairly empirical; perhaps it always will be. I think, however, that the work reported by Mr. Mead, wherein he has tried to evaluate the sintering variables and then interpret them in the light of what might be encountered in practice is very valuable. I would like to suggest that more papers along this line would be helpful contributions. Mr. Mead and his company are to be complimented on publishing this information.

E. H. ROSE—Recently the American Iron and Steel Institute had a meeting on sintering in Pittsburgh which I happen to have had the pleasure of attending and there were two representatives there from, I think, practically all of the steel companies throughout the country. There were two men from Bethlehem and two from Jones and Laughlin, a couple from Carnegie, Illinois, and a couple from our place down in Birmingham. Altogether there were some thirty men there in teams of two, one a research man and the other an operating man. There was a round table discussion to see what we could formulate in the way of a program in that organization to find out what we should do to approach within shooting distance of the very thing that Mr. Mead has brought out. It is quite clear that sintering, particularly in the fine sense, is a precision operation, or should be, and yet at that meeting we paneled all of the experts and asked them a lot of questions. We all resolved to do something more about that, and a program is getting under way which I hope will result in much more information on the whole subject. Now, the astonishing thing is that none of us at that meeting could even state what is good sinter. Of course, we are all seeking a sinter that will double the production of the blast furnace and all that sort of thing. No one could define it there. Perhaps someone can define it at this meeting. If so we certainly want him to tell us about it.

F. M. HAMILTON[*]—This paper on sintering variables is quite interesting to us and no doubt the rest of the industry. The sintering process is being more closely scrutinized and studied since more ores require agglomeration than heretofore, and it appears as though the trend will be accelerated in the near future.

We have expended considerable time and effort on sinter research in the past few years and much of our work has been along the same line as that of National Lead. Results are in agreement with those obtained by National Lead, although the approach to the individual problems was somewhat different in some cases, and different types of material were used.

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[*] Jones and Laughlin Steel Corporation, Negaunee, Mich.

In the case of the study of moisture control of the mix, our method was to make up different types of sinter mixes at various moisture contents and then determine the amount of airflow it was possible to obtain under fixed conditions through the mix without sintering. In this manner curves were obtained which showed optimum moisture contents for maximum airflow. Then mixes were made up with moisture contents on either side of the optimum amount and subjected to sintering tests. The time, in minutes, required to sinter a test batch of 35 lb was then measured by means of a continuous strip chart record of the exhaust gas temperature. It was found that the optimum moisture content varied with the material being used. For example, New York State magnetite from Benson mines gave the best airflow values at $7\frac{1}{2}$ pct moisture while fine Minnesota hematite gave the best airflow values at 10 pct moisture. Furthermore, the best moisture content for sintering was found to be just slightly lower than the optimum indicated by airflow tests.

In connection with pellets, I note that difficulties were encountered in sintering when pellets were unintentionally formed in the mixer. Our experience has been similar in this respect but we purposely made pellets in a pelletizing drum for sintering purposes. After many trials along these lines we conclude it is quite difficult to successfully sinter pellets made from fine materials. One of the reasons for the trouble appears to be the magnitude of the difference between the optimum moisture content for sintering and the minimum moisture content at which pellets can be formed.

Our work with the surface tension properties of water in the mix agrees with that of National Lead. Wetting agents are very detrimental to sintering; however, little success has been obtained by the use of oils, lime, or limestone with our raw materials.

As a result of experiments in the plant by our New York operators, fine fractions of coal were found to be detrimental to good operation. Best results in this plant are obtained on a No. 5 Buckwheat coal.

The authors of the paper emphasize the importance of the proper use of returns in sintering fine materials. Our laboratory work indicates that large size returns are a waste of good blast furnace feed and their use as returns in the mix is of little or no value in promoting bed porosity. We expect to be in a position to carry out production runs along these lines in the near future.

The present paper is both interesting and informative on a subject of great importance to the steel industry today. It indicates recognition of the growing importance of closer metallurgical control and better plant equipment for improved sinter operations.

T. E. LLOYD[*]—Concerning pellets, I think that both of you are right about pellets. When you attempt to sinter a pellet that is too large, very often the coal inside of it does not burn. More often it is roasted to a coke. In such cases, obviously, it is better to have this fuel on the outside of the pellets. If the pellet is small, air gets to the coal, it burns rapidly and you have a sinter.

You have probably noted that there is a remarkable difference in pellets. A charge in which the individual small pellets have been formed by rolling until they are free of air and are solid, (a good term is "dense") will sinter faster and more uniformly than a charge of identical proportions of moisture, fuel, and others, which has not been so carefully pelletized. I believe that in many of our arguments here regarding the sintering of pellets we must first take into consideration the physical qualities of the pellets. How good is your pelletizer or mixer? To add moisture uniformly is almost an impossibility, but how close does the pelletizer approach this goal? What is the specific gravity of your individual pellet?

A few years ago, the New Jersey Zinc Co. believed that a sintering mix could be benefited if it were squeezed by running through rolls before mixing. I do not know how far they followed this up but the idea is a step in the proper direction for two reasons. First, it tends to unify the moisture content. Second, it squeezes air out of the mix which in turn serves to densify the agglomeration of particles in the individual pellets composing the mix.

H. W. JOHNSON[†]—It is my understanding that the commercial plant is operating on a minus twenty mesh material now.

J. C. MEAD—That is right.

H. W. JOHNSON—With a bedding about 1 in., what is the screen size of your finished product and your weight per cubic foot of the product.

J. C. MEAD—There have not been any bulk density tests taken on the plus one inch sinter. There have been bulk density tests run on the return fines and they have been the following: 101 lb per cf on minus 1 in. plus eight mesh screen size, 99.4 lb per cf on minus $\frac{1}{2}$ in. plus $\frac{3}{8}$ in. screen size. The bulk density of sinter will vary widely unless some limits on screen sizes is followed which will exclude the "fines."

The screen size of the finished product is all plus 1 in. There have not been any screen analyses made, but by a visual check most of the sinter is plus 6 in. size with a maximum lump size of 2-ft pieces

H. W. JOHNSON—I think it would be a valuable addition to the discussion if that point were actually made—the weight per cubic foot—if there is a possibility of getting it. I think the importance of the weight of that material is of great significance. We have operated our furnaces on some test runs with high percentages of sinter with no improvement in operation. I think much of the reason for that is that we have failed to recognize the importance of the quality of the sinter used and one measure of this quality is the weight per cubic foot.

E. H. ROSE—I think that is quite true, Mr. Johnson; this also came out in Pittsburgh recently in a great many of our arguments about sintering. We can never get together because we cannot even define our subject. What defines quality? what is good sintering? In the investigation I mentioned a moment ago we are hopeful we will be able to set up some definitions. After all, just to say a sinter is hard or not hard or that it is bad or not good, very bad or very good, still does not say anything you can define and reproduce. It does not permit you to run a test with sinter as one specific definition and see what the blast furnace does and with another specific qualified quantity of sinter, what the blast furnace does on that.

Mr. Mead, did you make any porosity measurements?

J. C. MEAD—No, we did not.

T. E. LLOYD—First we know that iron ore at around 900 to 1000°C reduces two or three times faster than sinter of the same size. Secondly, it goes without saying that the structural or physical properties of iron ore fines in a furnace are impractical. Finally, it is known, but not often enough remembered, that sinter becomes increasingly more difficult to reduce as the carbon content, within practical ranges, increases. To me, the ideal sinter is a sinter coming from a charge so thoroughly and uniformly mixed that the practical range of fuel, say between 3 and 6 pct, can be held at its absolute minimum. Without the uniformity of thorough mixing, this range cannot be held. Either a trifle extra fuel is required to produce sinter or inevitably there will be portions of unsintered and channelled product.

When an ore is fine enough it can be pelletized. These pellets when roasted at around 900 to 1000°C are usually quite tough and contain about 40 pct voids. Not forgetting the difficulty of sulphur, and other elimination, if this could be done on a sintering machine I should think the resulting product would be even more ideal.

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[*] Newark, N. J.
[†] Inland Steel Co.

E. H. ROSE—Mr. Mead's mention of lime in his experiments only goes to remind me that in sinter, as in so many other affairs of this world, what is one man's meat is another's poison.

F. D. DE VANEY—I am a little bit reluctant to say anything about pelletizing. We are in the process of getting a full-size plant in operation, and one is reluctant to talk about something still to be done. The plant we have up in Aurora is a test plant in a way. In pelletizing or sintering the concentrates, we were interested in the most efficient and cheapest way. We rolled our concentrates up into balls and we learned a lot about that operation too. We rolled the material up in a drum about 8 ft in diam at a rate of 30 tons an hour, and the balls, when they came out, were hard. They would not stand shipping but they would stand movement around the plant. We fed these into what we call a tandem type furnace and then they were fired. We add our heat through a combustion chamber. The furnace is of the regenerative type, so our top gases come off at about 225°F and our pellets come out at the bottom at from 250 and 275°F. These pellets are hard when fired. I hope next year we will be able to prepare a paper and tell you just how the process works.

L. J. ERCK*—It surprised me a little to hear Mr. Mead say that the pellets which were made would not form a hard pellet on the grate inasmuch as they were a 100 pct pellet charged on a sintering grate. That point in my mind is just a little hazy now as to why the material produced in cake form would definitely sinter and yet the pellets would not. The material we are working with at the present is a straight hematite. We have found on several occasions that the fuel has to be very thoroughly mixed, and I mean thoroughly. The pellets themselves, if not thoroughly mixed, will vary, and if that is so you will find that one pellet will burn while the next pellet will be soft. Likewise, we found that each individual pellet almost has to be a thorough and complete mixture of the ore and fuel, for if it is not you will find that one part of the pellet will be soft and the other part hard. In respect to adding lime, that problem was brought up inasmuch as the concentrate on which we are working does not present enough of the minus 325 mesh size to form favorable feed to the balling drum. There must be a certain percentage which I believe we can be safe in saying is about 50 pct—at least 50 pct. I have seen a few tests at 40 pct but 50 is certainly more satisfactory.

We thought if we could add lime of minus 325 mesh proportion in the proper percentage, we would be doing quite a trick; we would not only be making up the deficiency of the minus 325 mesh but we would also be making something equivalent to a more or less self-functioning material. The material was prepared and placed in the pelletizing furnace and we ended up with a slag mass of about 900 lb that had to be lifted with a crane, and that ended that experiment.

A. C. RICHARDSON—What was the temperature?

L. J. ERCK—That is another point I might bring up. These materials vary. We just finished running a pelletizing test down at the station under which we had no control as to the moisture content. It was a filter cake with a very high moisture and in putting it through the balling drum all the material immediately formed balls. The new material added to the returns usually built up the said balls until they became of age. This was not the case. All the feed immediately formed balls from 1/16 in. up to about 1/4 in. so in placing that in the furnace we had to control the heat, not carrying it as close to the top as we usually do.

L. A. ROE—In our attempts to sinter pellets we used a batch sintering machine which was operated at a temperature of about 2475°F. Mr. Erck is speaking of firing pellets in a shaft furnace, and probably uses temperatures of 2000° or less. I wish to call attention to the fact that temperatures utilized to sinter pellets are considerably higher than temperatures used to fire pellets in a shaft furnace.

J. C. MEAD—What was the size of the feed you used in making the pellets, Mr. Erck?

L. J. ERCK—It has to be of proportion so that you do not diminish the quantity of minus 325 which is so essential for forming the pellets in the ball drum. You must be sure you have the proportionate amount of fines. Of course, the amount that you add in hematite is still relatively small.

E. H. ROSE—Is anyone familiar with the pelletizing operation at Santa Cruz on the cement?

G. J. HOLT—While trying to produce lump ore we used cement as a binder and almost everything from straw up and down. We were trying to produce lump ore. We ended up by deciding we did not know enough about it and gave up the entire project. Are you using a binder in your work?

E. H. ROSE—Yes. At the moment we are rather intrigued with the use of the paper mill waste. There are lots of paper mills in our vicinity, and we do have to heat treat it afterwards.

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The Influence of Temperature on the Affinity of Sulphur for Copper, Manganese and Iron

By E. M. COX, M. C. BACHELDER, N. H. NACHTRIEB, and A. S. SKAPSKI

DISCUSSION

(D. T. Rogers presiding)

D. T. ROGERS*—The conclusions drawn in this paper have important practical significance to the steelmaker and the metallurgist if, in practice, it is demonstrated that metallic copper in the charge will pick up sulphur from the furnace atmosphere and thus increase the sulphur content of the bath. The problem of residual copper arising out of increasing copper in the scrap available to the industry is, in itself, a matter of concern to the steel maker. If, in addition to the often detrimental effects of high residual copper upon the physical properties of some important steel grades, there is to be a complication of the sulphur problem, then we have a set of conditions that bodes no good for the open hearth melter and the open hearth metallurgist.

M. B. BEVER*—Investigations of gas-metal equilibria continue to be of interest, especially as new possibilities for improving experimental techniques emerge. Higher purity of reacting substances, better refractories, improved methods of temperature control and an increased awareness of the pitfalls of high-temperature equilibrium work are some of the factors that should contribute toward better data on gas-metal reactions.

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* Assoc. Prof. of Metallurgy, Mass. Inst. of Technology.

The authors have furnished adequate and interesting information on many aspects of their experimental procedure. A more detailed discussion of several factors, however, is desirable. The loss of hydrogen from the system by diffusion, thermal diffusion within the gas phase and the thermal decomposition of hydrogen sulphide may be named. Have the authors examined the composition of the solids after each experiment, and were both the true stoichiometric sulphide and the pure metal found to be present?

It is well known that hydrogen diffuses readily through silica at high temperatures and the same is probably true of other gases and refractories, although to varying extents. The authors' procedure of checking various furnace materials against each other is to some extent a safeguard against errors of this kind but the loss of hydrogen through silica should be acknowledged as an inevitable certainty. This loss can probably be tolerated since equilibrium between the gas mixtures and the condensed phases is likely to be maintained.

The use of an impeller for keeping the gas atmosphere in motion tends to eliminate the possibility of thermal diffusion, given a sufficiently high gas velocity, but this may in turn interfere with temperature equilibrium. The thermal decomposition of hydrogen sulphide is another potential difficulty on which further comment by the authors would be desirable.

Concerning the numerical evaluation of the results of this investigation the heats of formation evidently are based on an extrapolation over a temperature interval which is altogether too wide. It also seems very doubtful whether the scattering in the plot of the logarithms of the pressure against reciprocal temperatures is any less serious than the scattering of the free energy-temperature data which the authors have rejected as a means for evaluating entropies.

The authors concede that the interpretation of their results for the steelmaking process can be only tentative as far as the solid ingot is concerned. However, their interpretation of some fundamental features of the behavior of sulphur, copper and manganese in liquid steel is also open to question. They state that because of the relatively high affinity of copper for sulphur the sulphur content of the bath increases with the copper content of the scrap and that consequently the desulphurization process is hampered. This argument is equivalent to the statement that the presence of a deoxidizer in the bath raises its oxygen content and interferes with deoxidation. On the other hand it would seem to be consistent with the authors' point of view to expect that sulphur may be used to remove copper from molten steel. To avoid such conclusions it must be recognized that this investigation deals with pure substances and its results can be applied to the physical chemistry of steelmaking only by the rigorous methods of the thermodynamics of solutions.

R. E. MINTO* and H. B. EMERICK*—This discussion is aimed at the authors' principal conclusion, to wit: " . . . that metallic copper which is present in the scrap is to be expected to pick up sulphur from the open hearth furnace gases and thus raise the sulphur content of the bath."

An opportunity was afforded to test the validity of this conclusion in actual practice when during a recent period Jones & Laughlin Steel Corporation made 50 heats of 0.40 pct copper low alloy high tensile steel wherein the major portion of the copper requirement (all but minor final additions to adjust analysis) was obtained from high copper scrap charged with the regular scrap at the start of the heat. This scrap averaged 5 pct copper content, the copper being in the form of a heavy gild metal cladding and not as a copper-iron alloy.

A study was made to determine the effect of this added copper in the charge on melt-in sulphur and ladle sulphur chemistry. To do this, the routine sulphur and copper analyses on these heats were tabulated and compared with 50 heats made in the same period (and heat for heat chronologically as close to copper charged heats as possible) but with the practice of obtaining the copper requirement by the addition of pure copper late in the refining stage of the heat. This procedure assured reasonable constancy of lime charge and total sulphur content of the raw materials. The two practices are differentiated by calling the first group "copper charged" heats and the second group "copper addition" heats.

Preliminary copper tests are taken about 3½ hr before tap. Sulphur preliminaries are taken about 1½ hr before tap. When copper is supplied by pure copper it is added comparatively late in the heat—from ½ hr to 1¼ hr before tap. The heat at this time has been under slag cover for considerable time and subsequent absorption of sulphur from the furnace atmosphere is negligible. During the test period sulphur content of fuel oil ranged from 0.35 to 0.89 pct, averaging about 0.75 pct sulphur.

Pertinent data may be summarized as follows:

Practice	Copper Charged	Copper Addition
No. heats	50	50
Pct preliminary copper—Range	0.29/0.64	0.06/0.14
Avg.	0.38	0.09
Pct ladle copper—Avg.	0.41	0.38
Pct preliminary sulphur—Range	0.030/0.055	0.021/0.050
Avg.	0.0373	0.0363
Pct ladle sulphur—Range	0.023/0.038	0.023/0.034
Avg.	0.0271	0.0271

These data indicate that an appreciable pickup of sulphur is not experienced when about 1000 lb of copper is charged as high copper scrap in 175 ton basic open hearth heats melting down in about 4 hr in a furnace burning 0.75 pct sulphur fuel oil. No evidence is found to support the authors' contention that metallic copper present in the scrap may be expected to pick up sulphur from the heating gases, thus increasing the sulphur content of the bath.

C. E. SIMS*—I will not discuss the experimental work, not having gone into that portion of it closely, but let us assume that the figures are correct for the sake of argument and that copper sulphide is more stable than iron sulphide or even more stable than manganese sulphide at the steelmaking temperatures. It does not seem to me, however, that such a conclusion gives the authors the right to assume that copper, when diluted down to a fraction of a per cent, as is usually the case, could still exert an important effect on the affinity of that iron copper alloy for sulphur, or its ability to pick up sulphur from the gases. Now, if metallic copper is present as pieces of copper in the scrap, during the melting of the steel it probably would pick up a larger proportion of sulphur than the steel scrap and, of course, an important contamination of sulphur does occur during the melting. Even so, when it is present in such small quantities it does not seem that it could have an important effect on the total sulphur content. However, if it is true that in the finished steel the sulphides contain a large portion of copper sulphide then I think there is a significance that has not been touched upon by the authors. We know that copper steels give considerable trouble during the hot working of plate in the form of surface checking and edge cracking. In other words, in examining steel that has been hot worked and which shows this surface cracking we find that there has been a deep penetration of oxides along grain boundaries. Now, this occurs only during the hot working, and if a copper sulphide does constitute an important portion of the sulphides it may form a liquid eutectic at these hot working temperatures that would influence the penetration of oxide along the grain boundaries and cause this phenomenon of surface and edge cracking. This probably could be checked by finding the relative trouble from a high sulphur steel and a steel very low in sulphur but with about the same copper content.

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* Battelle Memorial Institute.

M. TENENBAUM[*]—I would like to confuse the role of copper and sulphur in the melting of plain carbon steels a little bit if I can. We make intentionally a good tonnage of steels containing over 1 pct of copper. Quite often we charge nearly all that amount of copper with the original solid charge and we have never run into any difficulty with any increased melt or final sulphur in this grade. Now, to confuse the situation, we often get complaints from our melters (and I am sure they have not read Dr. Skapski's paper) about the difficulty of removing sulphur from copper bearing heats, that is, heats containing 0.15 pct or higher copper in the liquid bath. They claim to observe this rather consistently and insist this condition actually exists. On reviewing our metallurgical reports in an attempt to get statistical evidence to support their observations, we have never been able to bring out any data that would indicate any increased difficulty in eliminating sulphur in the presence of copper.

N. H. NACHTRIEB (authors' reply)—The principal objection of Mr. Sims (supported by the evidence contributed by Messrs. Emerick and Minto) might be rephrased in this form: Is the thermodynamic activity of copper dissolved in liquid steel sufficiently high to remove sulphur from the heating gases and to fix it in the form of copper sulphide soluble in the steel? Our experiments give no answer to this question, inasmuch as they dealt with pure copper and iron with their respective sulphides, and not with copper at the level of concentration in which it prevails in actual steels. For the latter case the relevant chemical reactions may be written as:

$$4\ Cu + S_2 = 2\ Cu_2S$$
(in Fe)

and $$2\ Fe + S_2 = 2\ FeS.$$

The corresponding free energy relationships are:

$$\Delta F^\circ_{Cu_2S} - \Delta F^\circ_{Cu_2S} = RT ln \frac{(a_{Cu_2S})^2}{(a_{Cu})^4(p_{S_2})}$$

and $$\Delta F^\circ_{FeS} - \Delta F^\circ_{FeS} = RT ln \frac{(a_{FeS})^2}{(a_{Fe})^2(p_{S_2})}.$$

Whether copper is capable of competing with iron for sulphur under steelmaking conditions will depend upon whether $|\Delta F^\circ_{Cu_2S}| > |\Delta F^\circ_{FeS}|$. In turn, this depends not merely upon $\Delta F^\circ_{Cu_2S}$ and ΔF°_{FeS}, but also upon the activity of the copper dissolved in the steel, the activity of the copper sulphide (in the steel or in the slag), and upon the activity of the iron sulphide. We may consider the activity of the iron to be unity for all practical purposes. Since activity data are lacking, we cannot predict with any confidence that a fraction of 1 pct of copper in steel *will* result in an increase in the sulphur content of the steel as a result of reaction with the heating gases. The experimental evidence of Mr. Tenenbaum and that presented by Messrs. Minto and Emerick suggest that the activity of copper in steel must be *insufficient* to cause appreciable sulphur pick-up or to materially hinder the desulphurization process.

I should like to answer Mr. Bever's comments as follows:

Gas circulation, aided by the impeller, was estimated to be about 1 cm³ per sec. This, we feel, is high enough to overcome the Soret Effect of thermal diffusion. At the same time, it is probably low enough to permit the establishment of the equilibrium:

$$2\ H_2S = 2\ H_2 + S_2$$
in the hot zone.

For the highest temperature run with Cu_2S (1519°K) the experimentally determined $(H_2S)/(H_2)$ ratio has the value 5.15×10^{-3}. The pressure of sulphur vapor at this temperature is only 2.26×10^{-6} atm. (from Kelley's data for the thermal decomposition of hydrogen sulphide). This corresponds to only 0.044 pct decomposition of the hydrogen sulphide in the hot zone, and represents an error which is well within the errors in the analytical determination of hydrogen sulphide.

Mr. Bever is undoubtedly correct in stating that hydrogen diffuses through silica and other refractories at high temperatures. However, this introduces no error, since the measured ratio $(H_2S)/(H_2)$ is maintained by the metal-hydrogen sulphide equilibrium:

$$Me + H_2S = MeS + H_2.$$

Loss of hydrogen by diffusion through the furnace tube leads to a corresponding diminution in the hydrogen sulphide pressure.

Finally, Mr. Bever's comments comparing desulphurization and deoxidation may be examined. Elements serve as deoxidizers only if their oxides form a second phase whose solubility in the metal is low. Should their oxides be quite readily soluble in the metal, the oxygen content of the metal *would be increased*. Similarly, elements whose sulphides are very sparingly soluble in the metal should be effective in removing sulphur from the metal. To the extent that oxides (or sulphides) are soluble in the liquid metal the processes of deoxidation (or desulphurization) would be hindered; such elements might conceivably perform a disservice if their activities (and the solubilities of their oxides or sulphides) in the metal were sufficiently high.

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[*] Inland Steel Co.

The Role of Thermochemical Factors in Basic Open Hearth Production Rate

By T. E. BROWER and B. M. LARSEN

DISCUSSION

(H. C. Swett presiding)

L. REINARTZ[*]—In larger open hearth furnaces we have had somewhat different experience from Mr. Larsen. In the first place, we find a very considerable increase in speed of the heat if you lower the limestone charge, and furthermore, we have found a tremendous improvement in tons per hour by using heavier scrap iron in the charge. We have recently made some experiments in different ways to charge furnaces which have shown much greater regularity of slag run-off with about the same high percentage of pig iron being used. We have made heats containing up to as high as 70 or 75 pct of hot metal.

With this practice we have made some low carbon heats in very fast time. Some steel plants in the East have done very good work when charging light scrap iron because they are able to charge continually. In most plants where you must use light scrap iron, charging time increases very materially, and, as a result, the length of the heat time is very much increased.

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[*] Middletown, Ohio.

T. T. WATSON*—We have had considerable experience in all cold metal charging practice and examination of a large number of heats definitely indicated that the charging time is an extremely important factor affecting heat time. An increase in charging time will increase heat time. As the optimum charging time is approached the rate of flow of the raw materials (steel scrap and pig iron) is equally as important as the charging time.

M. TENENBAUM†—About six or seven years ago at Inland it was possible to relate our heat time with our limestone charge. About 1944 we mechanized our coal mines and we got a little poorer analysis hot metal as a result. We then found that we had to use quite a bit of our heat time in working sulphur. Accordingly, our limestone charges were increased. When we finally increased the stone charge uniformly throughout the shop, it was found that despite the increased limestone charge our heat time was not affected. When our practice was standardized to the point where we did pretty well on sulphur, we then dropped the limestone charge through the shop. Again we went back to the old condition where it did not make any difference. Apparently the time saved in pulling lime was lost in working sulphur. It is just a sort of warning that where you may save a few Btu's during melting you sometimes may lose more than you have gained. The loss can appear either as poor product quality or as increased heat time used to meet quality requirements.

B. M. LARSEN (authors' reply)—The comments here on the effect of heavy scrap, charging time, etc. illustrate the need for a more rational analysis of furnace variables in general. In melting down light or heavy scrap, we have (1) the "sharpness" of the furnace, (flame intensity, direction, etc.), (2) the rate of charging and the aggregate time with doors open, and (3) the amount of oxygen absorbed by each ton of scrap during melting. These factors are all involved in furnace speed and also are somewhat interrelated. For example, the more "sharp working" the furnace is, the faster will light scrap have to be fed in to avoid delay due to periods with charge down pretty flat and fuel reduced waiting for more charge. The advantage of heavy scrap will be greater with slow charging and also with charging conditions such that the furnace doors remain open an inordinate percentage of the charging time.

We cannot be sure even that light scrap always means more oxygen absorption, though that seems very probable in the average case. The point we tried to make in the paper was that more oxygen absorption from the gases means a lower net heat requirement by the bath; therefore, if whatever light scrap being used can be prepared and charged to the furnace about as fast as it can be melted down, with a minimum of open door periods, then we are *likely* to get faster production rate on light scrap charges. On the other hand, with the complex of factors above mentioned, it is easy to see the possibility of just the opposite effect, as mentioned by Mr. Reinartz. Also, dense piles of oily turnings or well compacted bales of sheet scrap might give a low amount of oxygen absorption, so that the detailed physical character of the scrap charge is probably involved.

Regarding Mr. Tenenbaum's comments, our experience has been that extra limestone does not always increase time of heat appreciably and this would be true especially where extra lime was needed anyhow for sulphur elimination; if it was not put in with the charge it would have to be added later so that the extra work in refining would offset any advantage from shorter melting periods.

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* Lukens Steel Co.
† Inland Steel Co.

The Interaction of Liquid Steel with Ladle Refractories

By C. B. POST and G. V. LUERSSEN

DISCUSSION

(*H. C. Swett presiding*)

J. STEVENS*—The authors state that the contamination in the metal was due mostly to the ladle refractories. Did the contamination vary with different brands of refractories or different qualities in the ladle?

C. B. POST (authors' reply)—That would be expected. In our shop we have used a grade of firebrick which is fairly standard. We do use high refractory nozzles to combat this erosion and high refractory sleeves, but there is such a problem when you get a skull in a ladle you just cannot use these high refractory bricks; you rip out the whole ladle getting the skull cleaned up. The acid bricks form a glass, and you can pull the skull out when you do get them. I believe you might find variations among the different refractories depending on how much silicon is in the brick. This determines how much silica is going into the interface between the steel and the brick. Our brick is about 35 pct alumina and 65 pct silica. With a brick of 35 pct alumina in the slag patches new calculations would have to be made.

R. PARDEE*—Where can you draw the line in determining the refractories as being a silica refractory?

C. B. POST—More silica than about 50 pct. I think perhaps that is generally the criterion. The brick we use is a good high grade fire brick.

T. S. WASHBURN*—With reference to the higher silicon that is recommended as a result of this investigation, is it contemplated that the specified range would be raised to 0.40–0.60 pct silicon, or possibly 0.50–1.00 pct silicon? These higher silicon ranges would affect the physical properties of the steel and consequently there might be some complications with respect to educating the consumers to accept this revision of the conventional analysis.

C. B. POST—It will take considerable work. Take AMS 6260 as an example. Ordinarily this specification calls for 60 or 75 manganese. Silicon has some hardenability in itself, and I believe if you aim for 40 to 60 for both the manganese and silicon you will have the same hardenability. At least, we have had no difficulty in meeting all the tests of the AMS 6260 specifications on that score. It might be if you had a steel too lean in hardenability for the job under the best of conditions you might get into a little trouble. I agree with you that it is going to take some work and by the people who are more qualified to talk on it than I. As far as I know, I do not think we will run into any difficulties in what work we have done.

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* Murray Refractories, Murray, Utah.

* Mexico Refractories Co.

* Inland Steel Co.

A. A. BRADD*—The authors present very interesting and valuable information about the effect of the Mn/Si ratio on the nonmetallic inclusion content of the steels investigated. However, another factor controlling the formation of the type of nonmetallic inclusion discussed by the authors is the composition of the ladle refractories with which the steel comes in contact before entering the mold. The authors' investigations were done with 65 pct SiO_2—30 pct Al_2O_3—5 pct Fe_2O_3 firebrick. Rait and Pinder in a paper on "The Origin and Constitution of Certain Non-Metallic Inclusions in Steel," published by the British Iron and Steel Institute in June, 1946, found that manganese alumino-silicate inclusions could be reduced to a minimum if the firebrick refractory with which the molten steel came in contact had at least 38 pct Al_2O_3. Their work was done with steels containing about 0.30 C, 2.80 Ni and 0.65 Cr, and Mn/Si ratio ranging from 1.68 to 3.87.

The harmful effect of higher Mn/Si ratios on cleanliness ratings might not be so pronounced if more aluminous refractories were used.

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* Ass't Supt. Treatment Dept., The Midvale Co.

The Ionic Nature of Metallurgical Slags. Simple Oxide Systems

By J. CHIPMAN and LO-CHING CHANG

DISCUSSION

(H. C. Swett presiding)

C. B. POST*—Just what are you showing that has not been shown by fixing the attention on molecular species and choosing the molecular species to give you a perfect solution?

J. CHIPMAN (authors' reply)—In general a fairly satisfactory thermodynamic treatment of slag-metal equilibria can be worked out on the basis of assumed molecular species in the slag. This has been the method used by Shenck and more recently by White. Winkler and I also used it in studying dephosphorization. Darken and Gurry found that it did not fit satisfactorily in the case of their data on iron oxides. The ionic formulas used here conform to the data much better and probably correspond somewhat more closely with the actual structure of the slags.

C. B. POST—It does seem to be similar to you?

J. CHIPMAN—It is alternative, and may lead to a more complete understanding.

C. B. POST—Have you had a chance to talk to glass technologists on this? Have they been using this type of set-up for glass solutions?

J. CHIPMAN—Yes, and the ionic formulas have given them a little better understanding of what liquid glass is like.

C. B. POST—Nelson Taylor always said we were going about slag reactions from the wrong viewpoint when using molecular species. Evidently the glass technologists use ionic species exclusively when dealing with liquid glass reactions.

J. CHIPMAN—I agree that it seems more rational and more accurate to use ionic rather than molecular formulas. We should be cautious, however, and not suppose that we really understand the structure of a slag just because we are able to fit its reactions by ionic equations.

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* The Carpenter Steel Co.

Discussion[*]

Extractive Metallurgy Division

San Francisco Meeting, February 1949

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[*] TP 2713 D.

Electrolytic Zinc at Risdon, Tasmania. Major Changes Since 1936

By S. W. ROSS

DISCUSSION

(*C. C. Long presiding*)

A. A. CENTER*—This paper reminds me of the beginning of the work of the Electrolytic Zinc Company of Australasia.

Early work for this Company, as some of you may know, was done at the Bully Hill Plant in California. After working there for some time Herbert Gepp, now Sir Herbert, came to the Anaconda Co. plants in Montana where I met him. He spent some months there, in fact almost a year if I remember rightly. That was when we were breaking in the new electrolytic zinc plant at Great Falls, Montana. From there he went back to Australia and started in on the plant there. I believe they had an original plant of about 20 tons per day of cathode zinc. We heard from them for some time, until they were able to go along on their own, and they have done very well ever since as you have beard.

Their practice, (the flow sheet, the leaching practice), has been quite different as reported in the paper and apparently they are still following that practice to some extent.

While the earliest work on selective flotation was done down in Australia, the big companies there, strange to say, were far behind the American companies in taking it up; and it is only in comparatively recent years they have gone to the alkaline circuit and dropped out thereby more of their iron and lead. The zinc plant now is up to a capacity of 100,000 tons a year and I believe that may be notched up to about 105,000.

T. H. WELDON*—I would like to ask

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* Consultant, San Francisco, Calif.

* Consolidated Mining and Smelting Co.

Mr. Gordon of the Risdon staff, whether, in the handling of these high sulphide calcines, there has been a build up of manganese in the solutions and if so how is it controlled?

A. R. GORDON[*]—Manganese has not built up tremendously. We have manganese in solution at present to the extent of about 18 g per liter. Removal in the cells by oxidation and losses in various incompletely washed residues and precipitates maintain a state of equilibrium. However the manganese content of feed solution has varied over the years from about 6 to over 20 g per liter. We have never had to take any special steps to control the manganese build up but if the amount increased unduly we would probably institute the discard of electrolyte virtually stripped of its zinc content.

L. P. DAVIDSON[†]—How much depletion do you have between your purified solution and your electrolyte when your manganese is that high? It will go in about 20 or 25 g per liter. What does your cell acid run?

S. W. ROSS (author's reply)—The removal of manganese in the cells varies chiefly according to the state of the anodes. New anodes will remove several grams per liter of manganese whereas old anodes, say over 12 months old, will remove less than ½ g per liter. On the average I would say we remove about 1 g per liter during passage through the cells.

C. C. LONG[‡]—Would some of the electrolytic zinc experts care to talk a bit about the removal of germanium and tin by means of soluble silica?

W. G. WOOLF[§]—Is the precipitation of germanium and tin by means of the soluble silica a chemical reaction or an absorption phenomenon?

S. W. ROSS—I do not think that anybody in Risdon has a very clear idea whether the removal is chemical or by absorption. I think the idea was that it might be absorption, but there is nothing definite.

H. R. HANLEY[*]—I understand that the electrolytic zinc plant at Risdon, Tasmania, makes 3-day cathodes at current efficiencies above 90 pct. In this country the stripping interval is limited to one day. Do you think that superior purification is responsible for the longer cathode deposition between strippings.

S. W. ROSS—Of course in thinking about the period of stripping you must remember the difference in current density too. We use a cathode current density of upwards of 30 amp per sq ft, whereas some of your plants in this country use appreciably higher cathode densities—I think as high as about 50 amp per sq ft. At the same time we have always believed that our ability to run long stripping periods has depended mainly on three factors, (1) adequate purification, (2) a suitable combination of addition agents, and (3) maintenance of reasonably low cell temperatures.

Purification is of paramount importance, and perhaps the most vital step is that in which limestone is added. It is not difficult to drop current efficiency by many percent by improper conditions of purification in spite of the fact that the iron is completely removed. Then it took us a long time to find what was apparently the best combination of addition agents. Under our particular conditions we have never improved upon the particular combination of glue and betanaphthol referred to in the metallurgical data of the paper. Any substantial departure from these amounts adversely affects current efficiency. Finally the maintenance of reasonably low temperatures is of great importance. We have often had parts of the cell room up to over 40°C with a distinctly adverse effect on efficiency.

I would say that solution purity is probably the major factor in permitting long stripping periods but other factors are important.

H. R. HANLEY—Do you think the soluble silica in the zinc solution at Risdon has any effect on the crystal structure of the cathode?

S. W. ROSS—I am not very sure about this. The use of soluble silica as an addition agent in zinc electrolysis is not uncommon practice and its presence is undoubtedly beneficial under the conditions in which it is used. At Risdon about ⅒ g of silica per liter survives the purification steps and enters the cells. It is quite probable that it has some influence on electrolysis and as Dr. Hanley has suggested it may affect the crystal structure. The way in which addition agents affect current efficiency and the structure of the deposit is a subject which has yet to yield many of its secrets. Much of the work done in the past has been somewhat on the hit and miss principle. We have carried out some research work on the structure of the zinc and its relationship to addition agents but I do not remember any attempt to link the effect of soluble silica with structure.

A. R. GORDON—Concerning the use of fine calcine in place of limestone for iron purification, I did not notice any reference to this in a quick look through the paper, but at Risdon we have often used fine calcine quite successfully and thereby reduced the requirements of sulphuric acid to maintain the sulphate content of the circuit.

S. W. ROSS—I note that our chairman referred to the removal of germanium and tin by means of soluble silica. I would like to draw attention to the point that no mention is made of tin in the paper in this connection. Silica appears to play an important role in the control of germanium but not of tin.

I thought that some remarks might have been provoked by the section of the paper headed "Roasting Policy." Risdon practice appears to differ widely from that employed by other plants in this regard and sometimes our roasting is looked upon as poor. However, the high sulphur oxidation per square foot of hearth area, achieved virtually in the absence of fuel addition, reduces both capital costs of the roasting plant as a whole and operating cost per unit of sulphur oxidized. On the other hand we have incurred the capital and operating costs of a flotation plant. The assessing of the debits and credits of this policy makes an interesting study.

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[*] Risdon Works, Tasmania.
[†] American Zinc Co., Monsanto, Ill.
[‡] St. Joseph Lead Co. of Pa., Monaca, Pa.
[§] Bunker Hill Co., Kellogg, Idaho.

[*] Rolla School of Mines, Rolla, Mo.

Cadmium Recovery Practice at the Donora Zinc Works

By G. T. SMITH and R. C. MOYER

DISCUSSION

(C. C. Long presiding)

L. P. DAVIDSON[*]—In the analysis of the cadmium sponge how is the sample prepared?

M. M. NEALE[*]—The analysis of the cadmium sponge?

L. P. DAVIDSON—You gave a very high percentage of metallic cadmium, 2 pct zinc, 2 pct lead and say 93 pct cadmium, or thereabouts. Just exactly how do you prepare a sample so that on a dry basis you get that analysis? Is that a dried sample?

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[*] American Zinc Co., Monsanto, Ill.

[*] Manager, Donora Zinc Works, Donora, Pa.

M. M. NEALE—Yes, that is a dried sample, but I cannot answer your question as to just how it is prepared. Our chemists do that and I do not follow that through.

L. P. DAVIDSON—With the cadmium sponge from our plant we find that the chemist will give an analysis of about 70 to 75 pct, and then if you analyze it completely there is about 10 pct that you do not find; if you put it in a combustion train and actually collect the water you will find there is around 10 pct water in what is ostensibly a dry sample. We found that by washing it with alcohol one gets a sample on a dry basis so that although a part of the cadmium may be oxidized on drying, it will figure to 100 pct. Without washing by alcohol we have not been able to get it,—that is why I asked the question.

M. M. NEALE—I cannot answer your question fully on that.

A. W. SCHLECHTEN*—I merely ask for information and I fear that in doing so I may reveal my own ignorance but the question is whether the addition of zinc dust alone effectively removes germanium from the solutions.

M. M. NEALE—I cannot answer that.

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* Missouri School of Mines, Rolla, Mo.

The Recovery of Cadmium from Cadmium-copper Precipitate, Electrolytic Zinc Co. of Australasia, Risdon, Tasmania

By G. H. ANDERSON

DISCUSSION

(*C. C. Long presiding*)

H. R. HANLEY*—I have been asked to discuss briefly the development of rotating cathodes for the electrolytic deposition of cadmium.

The earliest recorded use of rotating cathodes was by Hoepfner at Frufurt, Germany about sixty years ago. He electrolized zinc chloride solution using diaphragms to separate electrodes.

In the early experimental work of the Bully Hill Copper Mining and Smelting Co., Shasta County, Calif., rotating aluminum cathodes 4 ft in diam were used in the electrolysis of an acid zinc sulphate solution. Finished cathodes weighing up to 400 lb were produced. Because of mechanical difficulties, this type of cathode was abandoned for zinc, but was later used for cadmium because of the relative smoothness of deposit in comparison with stationary plates with comparable current densities. Cadmium sponge which forms on the cathode at moderate current densities (without special treatment) is entirely eliminated by a slow rotation.

The rate of rotation of the cathode has an effect on the mechanical nature of the deposit. A high rate of rotation concentrates the adhering electrolyte on the shaft; a moderate rate appears to concentrate on the cathode a short distance out from the shaft tending to corrode the deposit in the form of a ring. At a very slow rotation (2 to 3 rpm) the adhering electrolyte gravitates nearly vertically, thus avoiding the cutting ring referred to above.

The true explanation for the smoother deposits obtained on rotating cathodes may not be given definitely as the numerous factors involved are not thoroughly understood. Smooth deposits are obtained when the orderly growth of the metal crystals in the cathode lattice are disorganized. Thus the crystals form and grow for a very short interval when they are arrested and a new crystal forms. The continued growth of the original crystals provides large crystals and a rough deposit. Also if the acidity of the electrolyte is low, hydrogen gas bubbles adhere to the deposit. As the cathode is rotated the gas surface is brought into the atmosphere where they burst; thus the deposit is made on a surface relatively gas-free.

An aluminum hub distance piece was riveted to each aluminum disk 4 ft in diam, slipped on a 4½ in. steel shaft and pressed tight to prevent acid electrolyte seeping through to the shaft.

The 9-cathode assembly was supported on insulated bearings. Electrical contact to the shaft was made through what was equivalent to a copper pulley. Sufficiently high conductivity brushes were placed on the face of the pulley to lead the current to the cathode bus bar. The assembly was driven by a link belt contacting a sprocket insulated from the shaft.

The lead anodes were semicircular and supported on porcelain insulators placed on the bottom of the cell. Two anodes were provided for each cathode to permit an 8-in. space between them without increasing the ohmic resistance. This ample spacing permitted easy stripping of deposit with the assembly in place.

Cathode cadmium was melted under 650 W cylinder oil. After casting, the primary slabs were remelted under molten caustic soda and cast into pencils $^{11}/_{32}$ in. in diam.

Rotating cathodes for deposition of cadmium are used at Risdon, Tasmania, and at Magdeburg, Germany.

W. G. WOOLF*—This paper is very interesting to me because in our work at the Electrolytic Zinc Plant of the Sullivan Mining Co. we had an exactly similar problem—that is, a method of producing cadmium from our purification residue, the recovery of the contained copper as a copper precipitate which could be sent to a copper smelter and the production of merchantable cadmium. It is interesting to me, not knowing of the work of the Risdon people, how closely we approximate them in their main metallurgy, diverging at several interesting steps which I would like to discuss for just a moment.

For example, at Risdon they oxidize their purification residue. In our practice we take the current residue as it is produced in the purification department of the zinc plant and process it in the cadmium plant. The only oxidation that it obtains is the oxidation in the presses, the dumping of the presses and the collection and transportation of the residue to the cadmium plant.

We find that the leaching of that residue does not necessarily require the oxidation step that the Risdon people evidently find necessary.

The discussion of oxidation comes in again in the matter of the treatment of the precipitated cadmium sponge with zinc dust which again at Risdon is oxidized but which we do not attempt to oxidize except as it oxidizes itself in the storage. There is a partial oxidation which cannot be avoided, as Mr. Davidson pointed out, but we make no attempt to attain a complete oxidation and we dissolve the cadmium sponge in the sulphuric acid electrolyte of the electrolysis without any further oxidation.

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* Missouri School of Mines and Metallurgy, Rolla, Mo.

* Electrolytic Zinc Plant, Sullivan Min. Co., Kellogg, Idaho.

Coming to the question of the rotating cathode, I have discussed this a few days ago with Mr. Gordon who visited our plant prior to this meeting and asked him why at Risdon they had the rotating cathode. He mentioned one reason perhaps was that they started with it and they continue with it because it apparently gives them satisfactory results.

The second point was that in the long-time deposition as the cathode rotates, if there are any sprouts they are easily knocked off so they obtain a smooth deposit. As a result, they are not bothered with sprouting which is one of the difficulties of cadmium electrolysis. In our procedure we have stationary cathodes. Our cathodes are stripped every 12 hr which gives us a relatively thin cathode, but the thin cathode does not bother us very much in the melting procedure.

The difference in the melting at our plant and the Risdon plant is that we melt in an iron pot with electric furnace under caustic soda. There is relatively little oxidation. The amount of dross that we obtain is comparatively small and we find no need or requirement for the thick deposits such as Risdon obtains.

A. A. CENTER*—This matter of weathering the cadmium-bearing residue is rather interesting. When we did our early work at the Anaconda Co. on cadmium about thirty years ago, we found that the cadmium copper precipitate, which we had thrown out on the ground and left there while we worked out main electrolytic zinc plant difficulties, as a weathered product leached much more easily and we got a higher leaching recovery than we got with the current production. Mr. Woolf pointed out on the other hand that they do not find it necessary. It is somewhat a matter of product at each plant, and the prior operations leading to this product in each plant.

With reference to rotating cathodes, some of you may remember, but it may be news to others, that the electrolytic zinc plant built in Park City, Utah, about thirty years ago had rotating cathodes for electro-deposition of zinc. As I recall when I was there the plant was making about 7 tons a day of zinc with rotating cathodes. The capacity of the plant, I believe, was about 20 tons of zinc per day. This plant operated a few years but shut down when the price of zinc dropped off after the first World War and was finally dismantled.

A. R. GORDON†—Regarding the question of oxidation of cadmium precipitate we have done experimental work to determine whether we could leach the precipitate directly as it comes from the zinc plant and found that it was not as satisfactory as allowing it to oxidize first. As to why it should be so I do not know. We tried leaching it in acid with an addition of manganese mud to give oxidation in the leach, but even that was not satisfactory. Have you any explanation, Mr. Woolf, why there should be that difference in leaching?

W. G. WOOLF—The thing I neglected to point out in my discussion was the fact we return electrolyte from our cell room which carries about 270 g per liter as compared to lower acidity of your zinc electrolyte and I think perhaps that is the reason for it.

A. R. GORDON—Very likely that is the reason but we had heard about your practice before and tried out the straight leaching but in our conditions it was not satisfactory. There is another question I want to ask Mr. Woolf, what do you do with the trees that you scrape off your cathode cadmium in the cells?

W. G. WOOLF—As I pointed out we make only a 12-hr deposit and the deposit is quite free from trees and is dense and smooth.

A. R. GORDON—You have nothing to knock off to drop to the bottom of the cells?

W. G. WOOLF—No.

A. A. CENTER—I just want to say that the matter of the strong acid is not the whole answer, because, as I pointed out, our early experience at Great Falls was exactly the same as at Risdon, that the weathered material leached much more readily and yielded a higher recovery than the fresh product. Later we were able to leach fresh product with little drop in recovery using acid which was not much higher than before.

T. H. WELDON*—I do not know whether this will further confuse the issue or clarify it, but at Trail we more or less follow the same practice that Mr. Woolf mentioned was in vogue at Kellogg. We take our purification residue directly from our Shriver presses, pug it up and deliver it by pump to leach tanks with return acid. The leach pulp is circulated through the centrifugal pump and we think that a certain amount of aeration is introduced here which speeds up the leaching action. To finish the leach, we make sure that there is a slight excess of the cake. In that way, the copper is not taken into solution and yet a good recovery of cadmium is obtained. We then filter the leach to obtain a clear cadmium solution, and we use a very fine zinc dust in deficiency to precipitate high grade cadmium sponge. This particular sponge is delivered to the cadmium plant where, in the course of the operation, it is in storage for at least one week, and we think that some oxidation there is necessary.

Someone brought up a question of thallium. We have some thallium present in our ore which reports in our purification residue and that is taken care of in our purification of the cadmium electrolyte. If the purification is properly controlled, thallium is taken out in the residue. If it is not properly controlled some thallium will get over into our cells and at the time of cleaning the anodes in the cell, we will get a sludge in those cells that might contain up to 2 pct thallium. But as I say, normally that can be taken care of in the purification step.

Also, we are making a 24-hr deposit and we think the character of the deposit is dependent on the purification. If our purification is good we get good solid deposits with very little treeing, and the small amount of trees we do get are rolled up with the cathode and melted under a caustic slag. We make about a 98½ to 99 pct melting recovery.

A. R. GORDON—Talking about thallium, in what form is the thallium removed?

T. H. WELDON—If you remove any chances of reducing power in your finished leach and you purify the solution by a permanganate purification you will oxidize that thallium and precipitate it, probably as the hydroxide.

A. R. GORDON—Do you recover that at all?

T. H. WELDON—Not at present.

A. R. GORDON—What bad effect has thallium on the electrolysis if it is not removed?

T. H. WELDON—Principally in treeing.

A. R. GORDON—I mention that because our cadmium plant electrolyte has some thallium.

T. H. WELDON—A certain amount is deposited in the cadmium as well.

A. R. GORDON—Was treeing the bad effect?

T. H. WELDON—I think so.

H. R. HANLEY—Difficulties were found in cadmium electrolysis due to the accumulation of thallium in the electrolyte. This substance causes rough deposits and increases oxidation of the cadmium during melting. It was removed by adding sodium dichromate to the neutral cadmium solution, which forms an insoluble chromate of thallium impurity.

K. MORGAN*—Our practice at Avonmouth differs somewhat from that which has been outlined in the papers we have heard this afternoon.

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† Risdon Works, Tasmania.

* Consolidated Mining and Smelting Co., Trail, B. C.

* Imperial Smelting Corporation, Avonmouth, England.

We are smelters and are consequently afraid of all electrolytic processes. We follow somewhat the practice outlined by Mr. Neale. We take our sludges and Cottrell dusts from our acid plant purification system and extract these with acid. We take the neutral solution and precipitate arsenic by controlled additions of zinc dust. During this process we volatilize about half of it, leaving 50 pct in a residue containing an equal proportion of cadmium, which is subsequently treated.

We then take our solution and slightly acidify it. Incidentally we like to leave a little arsenic in at this stage, about 0.01 g per liter. We do not use zinc dust for our main precipitating stage but use zinc rods made from high purity zinc. These are agitated in trommels, which are rotary drums, the surface of which is formed of a wire mesh screen. We place the zinc rods inside the trommels and rotate them in the solution. We find this method gives us a very dense hard sponge which settles to the bottom of the tanks. It is periodically withdrawn and filterpressed and we find we can then melt it directly under caustic soda giving us a good yield of metallic cadmium.

The next stage depends somewhat on the purity of the metal. We use spectrographic methods and frequently find it is pure enough at that stage to cast directly into sticks or whatever is required. Sometimes the impurity content is too high and in that case we distil the metal in the furnaces somewhat similar to those outlined by Mr. Neale. If thallium is present, as it frequently is, we remove this by a melting treatment under zinc chloride. We built up a dross which contains up to 2 to 3 pct thallium. We recover this by subsequent treatment.

C. C. LONG—Mr. Morgan, what is the normal cadmium content of the solution from which the cadmium is cemented by these rotating zinc rods?

K. MORGAN—The solution runs about 100 g per liter zinc and 20 g per liter cadmium.

C. C. LONG—And the tail solution contains how much cadmium?

K. MORGAN—Our tail solution from the trommel agitators contains about 1 to 2 g per liter cadmium. We strip that cadmium by zinc dust treatment before returning the zinc liquor as a wetting down medium to our sintering plant.

L. P. DAVIDSON—What is the grade of the zinc with your zinc rods, and have you had any trouble with the cadmium forming on the rod and giving you essentially a cadmium coated rod that did not precipitate any more cadmium? I have seen that happen.

K. MORGAN—We make our rods of high purity zinc and find that by controlling the acidity and by keeping a very little arsenic in solution we overcome the trouble.

L. P. DAVIDSON—You want the arsenic to prevent the plating of the cadmium on the rods?

K. MORGAN—Yes. At first when we developed the method we tended to form dense coats on the rods which were very difficult to deal with. We found this could be overcome by leaving a little arsenic still in the solution. Nowadays we find quite often we can strip the arsenic entirely and still get no trouble; but as a general practice, we still like to leave a little arsenic in the solution.

H. R. HANLEY—In the production of sponge cadmium from cathode or slab zinc, it is necessary that the solution move slowly around the zinc.

Turbulent solution causes the cadmium to cement on the zinc surface and prevents further precipitation.

G. H. ANDERSON (author's reply)—Regarding the necessity for the oxidation of the cadmium copper precipitate before leaching, our first work nearly 30 years ago was on an accumulation of precipitate which had weathered in a heap for a considerable time.

This material leached easily and a high cadmium extraction was obtained but rather more copper dissolved than was desired. When unoxidized precipitate was treated it was found that the cadmium extraction was poor and insufficient copper was dissolved to insure the satisfactory handling of the cadmium precipitate in the latter stage of the process.

After various tests it was found that an oxidation time of 48 hr in open bins was the most satisfactory for Risdon precipitate.

There is no doubt that the composition of the precipitate affects its rate of solution. If small amounts of arsenic and probably other elements such as cobalt, are present, the solubility is increased and this is the most likely reason for the differing behavior of the various cadmium-copper precipitates. Risdon precipitate contains very little arsenic and cobalt.

This applies also to the high grade cadmium precipitate obtained later in the process.

At Risdon it has been considered good practice to control the oxidation of the wet high grade cadmium precipitate by applying a very low temperature to the material spread on a hearth so that a uniform product is obtained for subsequent leaching.

Our interest in the question of the oxidation of cadmium-copper precipitate was revived a few years ago when two of our staff returned from a visit to U.S.A. with the information that it was common practice to leach the precipitate without prior oxidation. Tests were conducted but it was found impracticable to obtain a high extraction of cadmium with a low finishing acidity in a reasonable time.

Referring to the revolving cathodes, it was found during the development of the process in 1922 that under the same solution conditions rotating cathodes could operate at a current density of 15 amp per sq ft whereas with stationary cathodes, a current density of only 7.5 amp per sq ft was possible over the same time of electrolysis.

Records show that in the early days of the plant, with apparently excellently pure solutions, it was possible to obtain regularly a current efficiency of 93 pct for a 96 hr stripping period with a current density of 15 amp per sq ft.

It is possible that the poorer results obtained in recent years are related to the presence of thallium.

During the early days of the plant, the whole of our raw material came from Broken Hill in New South Wales, Australia. This contained practically no thallium but now up to one third of our raw material is drawn from Rosebery, Tasmania, and this has introduced considerable quantities of thallium. As much as 20–30 mg thallium per liter is found in the cell feed solution but not more than 0.001 pct has been determined in the cadmium metal.

Also it was once the custom to purify the solution with $KMnO_4$, but this was discontinued because of the very slow filtering rate of the pulp and in its place was substituted the practice of discarding cell spent solution to rid the circuit of impurities.

Apparently the $KMnO_4$ purification is more necessary now than prior to the use of raw material from Rosebery.

Cadmium Recovery Practice in Lead Smelting

By P. C. FEDDERSEN and HAROLD E. LEE

DISCUSSION

(*C. C. Long presiding*)

T. J. WOODSIDE*—In the paper it was stated that many of the A. S. and R. plants probably used a process patented by Roscoe Teats in 1930. I might describe briefly that process as used at El Paso which I believe is typical of the four or five A. S. and R. plants at which it is used. Blast furnace baghouse dust carrying anywhere from 10 to 20 pct cadmium is mixed with approximately 20 pct slack coal and 25 pct fine limerock, charged into a Godfrey roaster, roasted at a temperature of 1500°F, temperature being measured through the arch of the roaster near the uptake, and the cadmium oxide fume running anywhere from 50 to 65 pct cadmium, the grade of the fume depending on the amount of cadmium in the feed.

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* Amer. Smelting and Refining Co., El Paso, Texas.

A. R. GORDON*—Regarding the practice at Port Pirie mentioned in this paper, I think that cadmium is no longer recovered as carbonate. It is not treated at Risdon as it was previously. It is some years since I saw the plant at Port Pirie and then cadmium was recovered as carbonate. Also I have not seen any published material describing their present treatment, but I believe it includes precipitation of the metal from solution by means of zinc, a method similar in some respects to that described by Mr. Morgan.

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* Risdon Works, Tasmania.

The Effect of High Copper Content on the Operation of a Lead Blast Furnace, and Treatment of the Copper and Lead Produced

By A. A. COLLINS

DISCUSSION

(P. C. Feddersen presiding)

H. R. BIANCO*—I should like to ask Mr. Collins if that statement he made about the addition of drosses to the blast furnace slowing down the blast furnace is a result of his own experience or a result of the experience of some older metallurgists; and perhaps I should ask him to define the type of drosses that he means.

A. A. COLLINS (author's reply)—That has been my own personal experience with dross. On various occasions at Chihuahua we attempted to incorporate the dross in our regular blast furnace charge and to shut down the dross reverberatory to try to save some money. As expected, we had very poor results. I think that Ed Fleming will well remember on one occasion, that was back about 1933, when we attempted the first experiment along this line, and as a result of the sulphur addition to the blast furnace to matte out the copper we ended up with hanging furnaces and mushy slags and abandoned the dross experiment, once again turning to the use of the reverberatory for handling dross.

H. R. BIANCO—Is that dross you refer to from the drossing kettle?

A. A. COLLINS—Yes, the dross that I am referring to came from drossing kettles. Furthermore, to back up my previous assertion, I had occasion in 1943, while up at Leadville, to once again experience the routing of dross through the blast furnace with its sulphur addition, since they had no dross reverberatory, and to observe that once the dross was removed, the furnace was speeded up almost 100 tons a day. All of these are personal experiences and I think that Mr. Feddersen also has had a little experience along this line—in fact, I believe all of us have had some experience.

H. R. BIANCO—I know at Trail they recirculate considerable dross through the blast furnaces and we also recirculate dross at Herculaneum and I am not aware that it has done much towards slowing down the blast furnace.

A. A. COLLINS—We have always had very poor results. In the first place you have got to add a sulphur addition to pick up that copper and once you do that, that sulphur is apt to combine with some of the zinc and you are going to form a little mush; before you know it you have furnace hangs and a poor working furnace. Now of course that depends on the amount of zinc you have on charge. But in 1943, Leadville had roughly about 7 pct zinc in their slag and it worked very poorly. Previously when they had 4 or 5 pct zinc in their slag it did not matter.

B. L. SACKETT*—At Tooele we had a great deal of experience with copper. We have always been able to keep a lead well, however, in spite of the fact we have run as much as 5 pct copper and only 15 pct lead on the charge. But regarding the handling of dross, our dross reverberatory furnace is only 7 or 8 years old. Before that we recirculated the dross through the furnace and thought we were doing a pretty nice job. Of course these things are all more or less relative—in other words you establish a certain condition much better than one of a few years ago and possibly as good as any other of which you know and you think you have pretty good results.

When we first took the dross off of the blast furnace and put it through the dross reverberatory furnace we immediately found out that we had gained something very real in furnace speed. Since that time there have been occasions when, because of the dross reverberatory being down, we have had to use dross again through the blast furnace and that has checked our original experience in slowing down the furnace very definitely.

So we feel that a dross reverberatory is a very valuable asset at the Tooele Plant.

A. A. CENTER*—Mr. Sackett's being here reminds me of trying to run with a minimum of lead concentrates the maximum of dross producing electrolytic zinc plant residue. He came up from International Smelting Co. to help us get started on that.

We took an old copper blast furnace at Great Falls, Montana, and made a lead furnace out of it by putting a lead well on the other long side which of course is a very unorthodox lead blast furnace. Our aim was to treat the residue from the electrolytic zinc plant, as I said, with a minimum of lead concentrates. That meant a maximum amount of dross. At that time selective flotation was not general practice, so our zinc concentrates ran relatively high in copper and other dross-producing elements; and of course these were largely in the zinc plant residue. I think we might call it muscle metallurgy, but we had an interesting, successful experience there and we ran for over a year thanks to Mr. Sackett's helping us get started. I have the details, but time does not permit. We did well enough so that the A. S. and R. Co. at East Helena kept boosting up the offer to us for the electrolytic zinc plant residue and there was not enough lead concentrate to supply two lead smelters there in Montana, so the matter finally finished up by the A. S. and R. Co. taking all of the residue under long term contracts.

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* St. Joseph Lead Co., Herculaneum, Mo.

* Tooele Smelter, Salt Lake City, Utah.

* Consultant, San Francisco, Calif.

The Use of Oxygen-enriched Air in the Metallurgical Operations of Cominco at Trail, B. C.

By R. R. McNAUGHTON, T. H. WELDON, J. H. HARGRAVE, and L. V. WHITON

DISCUSSION

(*P. C. Feddersen presiding*)

P. C. FEDDERSEN[*]—Mr. Weldon, how far do you think you can go on that? That is, how much oxygen could you use, what percentage?

T. H. WELDON (authors' reply)—That is the very interesting part of this investigation. The boys have just been theorizing a bit and it might be possible eventually to use pure oxygen in the zinc roasting in which case you could make 100 pct SO_2. Of course, you would have to redesign your furnace completely and have to supply a great amount of cooling to control temperatures. In some of the newer acid production methods where they use a cyclic process, 100 pct SO_2 would be very valuable. That would be an ultimate goal.

A. Y. BETHUNE[†]—What sort of zinc extraction do you get using the oxygen-enriched air in place of straight air in the roasting process? Does it change the leaching characteristics of the calcine in any way?

T. H. WELDON—No, I do not believe it does; actually with good roast using air only you will get, I think, as good a calcine as with oxygen-enriched.

A. Y. BETHUNE—Then in your opinion the application of oxygen enriched air or even straight oxygen would not have an adverse effect on the leaching properties of the calcine?

T. H. WELDON—No. We have run tests in our experimental roaster using as high as 50 pct O_2 and 50 pct air, and calcine produced is very similar to normal plant calcine.

C. C. LONG[*]—Mr. Weldon, you told us how use of oxygen in suspension roasting increases the capacity. At Josephtown we have the opposite problem. When operating on typical low zinc, high iron concentrates we find suspension roasters quite flexible as regards capacity. When operating on high grade concentrates relatively low in iron, operations proceed smoothly at 150 tons a day. However, if the feed rate is cut down to the order of 130 or 125 tons combustion is apt to cease. It occurred to me that perhaps use of oxygen-enriched air might enhance the flexibility when oxidizing such concentrates.

T. H. WELDON—That is a very good question. Actually I think the condition there is that an iron free zinc concentrate is lower in thermal value than a high iron concentrate. Also the ignition temperature is higher. In other words Sullivan concentrate with around 12 pct iron has a fuel value of 2200 Btu's. Some of these sphalerite concentrates will have a much lower Btu value, in the order of 1800 Btu, therefore heat is not available there to maintain ignition temperature, if radiation losses are constant, or if excess air or moisture is present. I quite agree with you that a low iron concentrate is a little harder to handle and the value of oxygen-enrichment would be greater with that type of concentrate.

I did not mention that we also roast iron concentrates for the production of SO_2 for our acid plants. This iron concentrate is a pyrrhotite. In the case of the iron concentrate a larger percentage of the oxygen is tied up as metallic oxides and the theoretically possible SO_2 is only around 10 pct. Since theoretically possible SO_2 concentration is about 10 pct, if you require high gas strength, oxygen-enrichment is of much greater value there.

W. F. JOHNSON[*]—I would like to mention in connection with Mr. Long's question, that I did some work 10 years ago in oxygen-enrichment and found that the ignition temperature was considerably lowered with a slight increase in oxygen content so that it probably would require a much lower temperature to get ignition, and the furnace would not go out so readily.

L. P. DAVIDSON[†]—In answer to Dr. Long's question about suspension roasting of low iron concentrate, we had a concentrate which we roasted successfully that had less than 2 pct iron. The only way we could roast that and get good tonnages was to updraft our furnace. We sent those data to Trail, but I think we were considered heretics.

Frankly, I like a suspension roaster that is updrafted. You can, if you want to, put some air in on the bottom hearth to finish off those last few traces of sulphide sulphur, and your updraft will permit you to do it. We were limited on the tonnage we could treat, we had no waste heat boiler and had to take our gases to a chamber acid plant. We had to keep the temperature up to get sufficient concentration in our glover tower by updrafting the furnace. Taking the gas off from the top of the combustion chamber instead of down on the seventh hearth enabled us to increase our tonnage, decrease the sulphide sulphur in the calcine and we had a much better working furnace.

Our dust loss, that is the collection in the cyclone, was no greater than when the furnace was downdrafted.

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[*] Bunker Hill Smelter, Kellogg, Idaho.

[†] Sullivan Mining Co., Electrolytic Zinc Plant Kellogg, Idaho.

[*] St. Joseph Lead Co., Josephtown, Monaca, Pa.

[*] Amer. Smelting and Refining Co., Selby Calif.

[†] Amer. Zinc Co., Monsanto, Ill.

Concentration of the SO_2 Content of Dwight-Lloyd Sintering Machine Gas by Circulation

By W. S. REID

DISCUSSION

(*P. C. Feddersen presiding*)

R. R. McNAUGHTON[*]—The Smelting Co. and Mr. Reid and his men at Selby are to be congratulated on the job they have done on sinter gas recirculation. I think it is not going to be very long before most companies that have a sulphur dioxide emission problem will realize that they must collect and fix that sulphur some way.

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[*] Consolidated Mining and Smelting Co. of Canada, Ltd., Trail, B. C.

T. E. LLOYD*—Between the windboxes, did you have dead plates?

W. S. REID (author's reply)—Not a dead plate as such. Ordinarily we think of a dead plate as a solid cast iron plate some 20 or 22 in. wide. Between our windboxes in the recirculation units there is a light plate, flat shaped but tapering off at either end; just an umbrella, we call it. It does prevent passage of excess air which otherwise would pass through the ribs of the pallet.

T. E. LLOYD—Just between the pallets?

W. S. REID—Wide enough to extend between two ribs of the pallet.

T. E. LLOYD—I was interested in the fact that you cool the gas there and then abandon it. The Tennessee Copper Co. at Copperhill, Tenn., are cooling a terrific amount of gas. Would you probably succeed better if you took the considerable amount of moisture out and recirculate the gas? What did you notice in the difference when you were running it?

W. S. REID—There are advantages in cooling and also in taking the moisture out, but our problem was entirely a practical problem. By getting the ducts cold, especially due to the periodic operation of Dwight-Lloyd Sintering Machine wherein you must close it down periodically to clean the windboxes, any moisture you get into that flue system just corrodes it greatly. It went out on us in a short time. We then tried stainless steel flues, and if the moisture is in there they go out just the same. We eventually wound up by using a lead flue from our second-over machine which is used periodically only. Lead itself stands up all right, but the expansion and contraction broke the lead flue so we were constantly welding the flue to keep it from leaking SO_2 into the building. We have eventually wound up by using wrought iron, as our tests show that wrought iron, insulated to keep the pipes warm all the time, presents no serious corrosion problem. Cooling causes condensation of moisture and the flue goes out in a hurry.

T. E. LLOYD—You spoke of segregation, do you mean you attempted to put the charge on the pallets in such a way that you did not even have a segregation on the pallets?

W. S. REID—No, it is exactly the reverse of that. We want the segregation there, that is, a uniform segregation of the coarse material on the grates to form a grate dressing. Major segregation of coarse and fine from the feed hopper itself is bad. If the feed can be kept flowing uniformly out of the feed hopper, then by close regulation of the talus pile, there will be a uniform rolling of the coarse particles to the grate with no sluffing, and no slides; then a uniform bed throughout the machine will be obtained and that ties right in with the concentration of gas.

T. E. LLOYD—You found it necessary to have fresh air come in from around the muffle?

W. S. REID—Immediately in front of the ignition muffle until the bed is well under way on ignition and burning well.

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* Engineers Inc., Newark, N. J.

Autogenous Roasting of Low-grade Zinc Concentrate in Multiple-hearth Furnaces at Risdon, Tasmania

By J. A. B. FORSTER

DISCUSSION

(P. C. Feddersen and T. D. Jones presiding)

W. G. WOOLF*—The paper has a wealth of data that take careful, detailed study. As has been indicated the highlights can be only touched in the paper. The design and the arrangement of the rabble teeth as well as some of the other details of operation show a very careful study and a scientific approach to the problem which in most plants using hearth roasters are matters of trial and error with empirical conclusions and, perhaps too often, just arbitrary supervisory preferences which may be erroneous. Here the problem has been approached from a scientific angle which I think well merits careful study. The ability to treat the tonnages they get through these furnaces I think is made easier by reason of the high sulphide sulphur in the resulting calcines which the balance of the plant—the leaching and so on—can cope with.

As indicated by Mr. Weldon in his discussion earlier this morning, in most zinc plants an attempt is made to have as low a sulphide sulphur content in the roaster calcine as possible. But in the operation of the Risdon plants, they are able to cope with sulphide sulphur content up to 5 pct which is far beyond the amount of sulphide sulphur that can be handled elsewhere. I think the autogenous roasting is made easier because driving out the last percentages of sulphide sulphur brings on the necessity for extraneous heat, and that is further exemplified because even at Risdon the author shows the desirability of using some oil to better the operation, particularly for uniformity of roasting results and to obtain more regularity of furnace operation.

A. A. CENTER*—Regarding the hard crusts in the beds of the furnace and autogenous roasting, the paper speaks of the former being due, at least to a considerable extent, to lead sulphide in the crusts. I wonder if the author has considered the hard crusts as being due in large part to zinc sulphate. While I was developing large zinc operations we ran into hard crusts which had to be dug up. I took several lumps which were so hard they showed the marks of the rabble teeth very plainly and kept them in my office for some weeks. A visitor came along one day, and as he was having similar troubles, I told him what we were doing about ours. I started to pick up one of these lumps and to my amazement the thing crumbled in my hands whereas originally it had been so hard it wore the rabbles down very rapidly in the furnace. I sent the sample to the laboratory and found that it analyzed very high in water-soluble zinc and sulphate-sulphur. The crumbling of the lumps was evidently due to the anhydrous zinc sulphate gradually taking on moisture from the air and forming crystalline zinc sulphate seven parts water. The increase in volume would, of course, result in disintegration of the lumps.

As to getting a high tonnage in the autogenous roast, that is partly because of finishing at about 5 pct sulphide sulphur. It is a real job to get down to, say, ½ pct sulphide sulphur, which is what is usually desired, and still put through a good tonnage.

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* Bunker Hill and Sullivan Co., Kellogg, Idaho.

* Consultant, San Francisco, Calif.

Autogenous, multiple-hearth roasting of zinc concentrates usually yields calcine analyzing not much under 5 pct sulphide sulphur. For example, a lithopone plant which had been used to treating only zinc wastes bought some calcine, immediately ran into troubles, and called me in. On finding where they were buying the zinc calcine, I knew they were getting calcine produced from zinc concentrates in an autogenous, multiple-hearth roaster operation, and that the calcine would probably run around 4½ pct sulphide sulphur. This proved to be the case in spite of several disclaimers.

It is to be noted that the above discussion was sent in at the request of the AIME staff, and is based only on the abstract of the paper as heard at the San Francisco meeting.

J. A. B. FORSTER (author's reply)—Mr. Woolf is quite correct in thinking that the means used at Risdon for recovering unroasted sulphide from calcine make it easier to obtain very high roasting rates. Advantage has been taken of this at times to make up for shortage of roasting capacity by tolerating an uneconomically high sulphide sulphur in calcine.

The Risdon provision is unique in being a flotation unit which returns to the roasters a concentrate that can be roasted autogenously. It is not unusual in other roasting plants to screen the calcine, crush the oversize and re-roast it, either alone with the assistance of extraneous fuel or mixed with new concentrate. In such cases the calcine assay quoted is usually that of the screen undersize. It is not easy to compare the performance of a roaster treating low grade concentrate and delivering unscreened calcine with one working on high grade concentrate and screening the product, but the sulphide in Risdon calcine is mainly in the coarse fraction.

By sacrificing some roasting capacity to give the material longer time in the furnace, the sulphide left in the coarse fraction can be reduced considerably, but in this case so little heat is evolved in the lower hearths that extraneous fuel is needed to maintain roasting temperature. This has been a common practice.

Additional roasting time can be given in the lower hearths by modification of rabble teeth; and since more roasting is then done in these hearths, the amount of extraneous fuel needed is less. The author hopes to demonstrate at a later date that, by carrying modification of the rabbling system to the logical conclusion, a very thorough roast can be obtained at a high hearth rate, and strictly autogenously.

Dr. Center's observations are correct, insofar as they went. There is a great difference in conditions if the space between hearths and teeth is filled with material partly roasted or with sand. In the first case, if the immobile beds are not hand-stirred every two or three days they become so hard that heavy bars and hammers are needed to chisel them. In the hottest zone where the material still contains much sulphide there is little or no sulphate formation, the binding of the bed being due to the condensation of galena vapor from the mobile bed, galena having a vapor pressure of 2 mm at 850°C and 4 mm at 920°C. Galena also condenses on the teeth which are cooler than the mobile bed, and the resulting drag on the hard hearth cake can stop a furnace or break rabble arms. Of course a galena-free concentrate would behave quite differently in these hearths.

It is in the lower hearths, where the material is much more completely roasted and temperatures are well below that of its decomposition that zinc sulphate forms in the immobile beds. Sulphation is accompanied by expansion of volume and there develops an upward pressure against the teeth which is just as damaging as the drag in the hotter hearths.

When the immobile bed space is filled with sand the conditions are somewhat different. In the hotter hearths galena vapor still penetrates the bed causing some consolidation, and galena crusts are formed on the teeth; but provided the latter are replaced by clean ones every two or three weeks no drag develops until the bed is fully consolidated—a process which takes over three months if excessive temperatures are avoided. Owing to changes of temperature in hearths, columns and rabbles, and to growths on teeth, some sand is lost from the bed surface and is replaced by a crust similar to ordinary hearth cake, but as long as the crust is relatively thin and there is some unconsolidated sand below, no trouble occurs.

In the lower hearths the crust which forms in the same way is quickly sulphated, but as it is very thin no noticeable drag develops. The crust thickens slowly, and it is probable that under slight pressure some sand is gradually squeezed out laterally, but the beds remain in good condition for at least nine months, except around drop-holes and close to the walls where necessary cleaning results in loss of sand; consequently these beds are renewed twice a year.

Development of the Modern Zinc Retort in the United States

By H. R. PAGE and A. E. LEE, JR.

DISCUSSION

(L. P. Davidson presiding)

A. E. LEE, JR. (author)—In addition to the paper we should like to make a few remarks. First, the seriousness of bending of the clay retort cannot be overemphasized. Not only did bending limit the length of the vessel, but it permitted corrosive fluid slags to concentrate in the belly of the retort and thus increased the possibility of boring. Bending also practically prohibited the use of cleanout machines and increased the danger of excessive fume losses by allowing furnace gases to escape around the top of the retort mouth.

It will be noted that the Blackwell pottery practice places considerable emphasis on careful drying of retorts. Perhaps it is another smelter superstition, but traditionally the aging of retorts beyond a reasonable drying period has been considered important to long life. We are unable to give a good explanation of why aging should improve retorts. During the past fall in an attempt to prove a theory that the combined water in the clay decreased during aging, about 50 samples of wet retort collars were placed in a dry room when it was closed. Loss of weight, combined water and free moisture were measured each week over the 100 day drying period. The affinity of the dried retort for moisture makes difficult the accurate measurement of free water; however, there was a clearly defined free moisture change from about 12.5 pct when freshly made to about 2 pct at the end of 18 days, then a gradual loss to about 0.25 pct at 70 days and an apparent equilibrium near this figure through the 100th day. There was no appreciable change in the combined water. The change in weight of the average sample was, however, rather unusual, there being consistently a loss of weight throughout the entire 100 days. From the 63rd day on this leveled off to about 0.03 pct per week. These were small samples and certainly should have dried somewhat faster than the larger retort. Possibly the drying process continued although at a very low rate during the last 30 to 40 days and this caused the weight change, but our method of determining free moisture was not accurate enough to record it. In any event we have concluded that our test did not show any evidence of change in structure through loss of combined water.

An important characteristic and defect of the silica retort is its inability to withstand sudden temperature change. This is very important in starting up a furnace block. Until recently we had started a new block by filling it with green dried retorts, lighting the drops at a minimum gas setting and gradually bringing the new brickwork and green retorts up to a charging temperature over several days. This is, of course, a delicate operation and it is most difficult to hold the gas flames so low at the start as not to touch any of the retorts, especially those in the second row. We averaged a loss of at least half the original retorts during the first 3 or 4 charge cycles. A major cause of retort failure was checking about 2 ft from the mouth where the tip of the flame had touched the retort during the period of low gas firing. Recently the idea was conceived to close up the front of the furnace with butts and bring up to about the heat of a retort preheat kiln; then put in hot retorts. This method has been used on the last 3 blocks started with excellent success. The extra labor required has been more than offset by savings in retorts and by achieving normal recoveries several shifts earlier. An opportunity is afforded to measure accurately the life of the original 800 retorts and this was done on the first block started in this manner. The average life of the 800 original retorts was 34.23 cycles compared with 26.43 for all retorts in all our furnaces during the same period.

ARTHUR D. TERRELL*—That paper just given is exceedingly interesting. You only have to look at me to know that I can go back in history further than my Blackwell friends. As regards the first retort presses used in this country, they were I believe installed by the New Jersey Zinc Co., one of them at Bethlehem, Pa., and the other at Joplin, Mo., the old Empire Zinc Co. I became identified with the zinc industry in 1899 and went to Iola, Kansas in 1900 with a Mr. George E. Nicholson who sold his plant to the New Jersey Zinc Co. and I remained with it for 22 years.

These presses were installed about 1898. They were abandoned as far as those plants were concerned, and one of them was shipped to the Prime Western Spelter Co., Iola, Kansas, plant about 1903.

As regards the oval retort, they are used not only for increase in strength due to the type of cross-section, but the heat penetration is better.

My recollection is that in a number of horizontal retort plants in the early days, a pottery consisted of two floors: one, where the retorts were made and were set on that floor for a few days until they got dry enough to be handled; then they were elevated by a one-retort-capacity hand elevator and put on the second floor, remaining there until they were taken out for use in the furnaces.

A small percentage of the zinc that goes into the walls of a fire clay retort, forms spinel.

With regard to the carborundum retort, I was with the New Jersey Zinc Co. when they made the first ones at Palmerton, Pa., and followed the results fairly closely. They were tried at some of their other plants, but never were permanently adopted as far as my knowledge goes.

The National Zinc Co., Inc., Bartlesville, Okla. made a test run on silicon carbide retorts several years ago, but did not continue their use. There have been some very unfortunate experiences and very expensive ones with the trial of carbide retorts. One of the difficulties, I believe Mr. Lee has not touched upon is the question of keeping down the blistering on the outside, particularly where you use natural gas as a firing fuel. That not only tends to weaken the retorts but makes it very difficult to get them out of the furnace after they have been in service for many months.

As far as making the retort is concerned, the indicated pressure we use for making the butt of a retort is between 2000 and 2500 psi, and the pushing out pressure is about 1200 psi. Of course, I do not think those refer to the pressure Mr. Lee has in mind. Now it is true that it seems advisable to dry clay retorts for a minimum of 30 days, unless accelerated drying is used. However, I will mention one experience we had with one of the New Jersey Zinc Co. plants at Collinsville, Okla. It had just been started the year before I became connected with it, and it grew faster than the pottery capacity did, and we got down to a 10-day life of retorts in the pottery. I confess I was very much disturbed thinking that we might have to dead fire some blocks in order to catch up on our retorts. But we ran that plant for a little while on retorts that were dried only about 10 days until we could get more rapid production of retorts which we did by putting in a new pump and a Simmons valve. Our hydraulic press capacity was then about 250 retorts in an 8-hr day instead of about 100 retorts.

As regards starting up a furnace with silica flour retorts, our experience has been just about what Mr. Lee's company's experience has been, and we had some very unfortunate results in high loss of retorts. The next time we start up a block of furnaces we are going to do about the same as Blackwell has done.

A. E. LEE—One thing I forgot to mention is a printing error in the first sentence of this paper. That is the date when commercial scale use of horizontal retorting began in the United States; that should be 1860 instead of 1890. It is interesting to note that Matthiessen and Hegeler at LaSalle, Ill. have been operating since 1860.

K. MORGAN*—It is a little difficult for me to comment on Mr. Lee's paper because our practice today at Avonmouth and also, I think, throughout Europe generally, differs in almost every respect from that outlined by Mr. Lee.

For instance it appears to be the general practice in the States to use either the silicon carbide type of retort or the silica flour type. We do not use either. We use an all clay mix. Then again on the question of de-airing, we have tried de-airing, but do not find it gives us any advantage. On our standard mix we use Belgian clays. During the war, for obvious reasons, we could not get Belgian clays and we had to use English clays. These have not the plasticity of Belgian clay and with them we do find we get some advantage from de-airing, but on Belgian clays there is no advantage at all.

There are a number of other difficulties which I am afraid would take up too much of your time, but I should like to make a few points:

The first is on this question of life. Figures for life can be very deceptive. You need to know the amount of zinc that is produced, since if you do not drive your retorts, you can get almost what life you like. It is only when you are pushed for output and have to strike a balance between output and life that life figures become significant. I should like to know from Mr. Lee how much zinc he makes per day from each retort. Our retorts are fairly big. We make about 77 lb of zinc a day from each retort. At the moment we get about a 27-day life and while we are always trying to improve it we have not been able to do so without being prepared to drop output.

The next point on which I should like to have Mr. Lee's comment and also that of the previous speaker is on the question of holing. We have to use ores containing anything up to 14 pct iron. The reason why most of our retorts fail is due to holing and when this occurs we find it is generally associated with laminations in the retort. We think that if we could stop the formation of laminations during extrusion we could greatly reduce our retort failures.

A. E. LEE—In answer to your first question about the life of the retort in terms of zinc produced, I agree this is a more accurate criterion than days. We do not figure it in terms of zinc but in terms of retorts per ton of sinter or zinc-bearing material charged. In recent years we have gotten about 0.6 retort per ton of sinter.

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* National Zinc Co., Bartlesville, Okla.

* Imperial Smelting Corporation, Avonmouth, England.

I believe that the clays you have in Europe are somewhat more refractory than the ones we have available here in the States and that they withstand a higher temperature without bending. That perhaps accounts for your success with the straight clay retort.

Insofar as slagging is concerned, we have had some bad experiences with ores running as high as 12 to 15 pct iron. With ores of this character we have found retorts with the bottom half filled with a very hard iron slag after a period of several shifts.

As you point out, boring or holing occurs with furnace charges containing appreciable amounts of iron. This effect can multiply retort losses when the fluid slag drips down on retorts below. We attempt to control this by close firing so that during the latter part of the furnace cycle the charge is not so barren that the heat absorbed can be used to make the slag active.

Regarding laminations, we do not have much of that. We think perhaps this is one of the advantages of our de-airing pug mill.

L. P. DAVIDSON*—Mr. Morgan, in your slagging troubles are they all attributable to iron alone or do they become worse with a larger amount of lead?

K. MORGAN—No, I do not think we ever attributed trouble to lead. In every case we find the corrosive slag is an iron silicate.

L. P. DAVIDSON—It is not due to the formation of a very fluid lead silicate?

K. MORGAN—Not in our experience.

A. D. TERRELL—I might say we have at times gotten over 85 lb of zinc per retort. Most of the smelters are using the 48-hr cycle now and you do not reach as high top temperature to work off furnaces as you do on a 24-hr cycle, and that makes a difference in life of retorts.

C. R. KUZELL†—It has been very refreshing to hear this paper in a field of metallurgy that most of us in other fields of metallurgy were always led to believe was rather stagnant. From what I am able to gather, having heard from some fellows of the modern-day cost of building electrolytic plants, it looks as if we are still going to be confronted with dealing with retort plants for some time.

Since we on the selling end are interested only in the question of zinc production to the point of producing zinc concentrates and selling them to these retort and other plants, of course the matter of retort life is of interest. We are often irritated by those settlement sheets showing the high penalties for iron and other fluxing impurities which cause a failure of these retorts about which we have been hearing. Consequently I have three questions which are prompted by ignorance, curiosity, and selfishness—by ignorance because I have never seen a zinc retort, by curiosity because I am naturally curious, and by selfishness because of the irritation that arises from seeing these high deducts.

I would like to ask three questions: (1) What is the porosity of these retorts? (2) What is the relative loss of zinc through the walls of the retort? (3) Why have they never made retorts of basic refractories? As the basis for answering the question I would like to specifically recommend the hypothetical use of chemically bonded periclase subsequently burned and then used as a retort.

A. E. LEE—I do not know of any figure for retort porosity as such. However, we do have figures on the amount of zinc absorbed in the retort walls. As previously stated this was 7–9 pct of the retort weight with clay retorts. At Blackwell we recently assayed used silica retorts with a furnace life of about 26 cycles and found only 0.9 pct zinc. It has also been estimated that 2 pct of the zinc in the charge was lost through the walls of clay retorts and this is borne out by the deposits in the regenerators of some of the old producer type of furnaces. But I do not know any figure to give you on the carbide or silica retorts.

In regard to use of other refractories, I would say off hand that they might have the same failing as the early cast carbide retorts—they cannot stand the heat shocks. I would like to know what Mr. Terrell might think on that subject.

A. D. TERRELL—I feel what Mr. Lee has said would be the difficulty. They would not stand the thermal shock.

C. R. KUZELL—I would like to point out that four decades ago the copper industry in bessemerizing copper matte for the production of blister copper departed from clay and silica linings and adopted basic linings of magnesia. In some of the more recent years some of the plants have used periclase, which is a purer magnesia—purer than formerly used in magnesite brick. That has been used in the form of rammed linings and also in the production of the bricks where bricks continue to be used. The converting process is also cyclical and subject to thermal shock but nevertheless the use of the basic material has been highly successful. It would seem to me that if those who get penalized for excess iron in selling zinc concentrates would use a basic refractory like magnesia which would not be corroded by the iron and other fluxing constituents of the concentrates maybe we would be better off and get rid of some of those deducts.

A. E. LEE—There has been some experience with that type of lining. In 1900 Benjamin Sadler patented a non-corrosive retort lining. The lining consisted of magnesia, chromite or carborundum which was ground to pass a 20-mesh screen. A regular dried retort was coated on the inside with sodium silicate. Then the ground lining was added and the retort rotated until a uniform ⅛ in. lining was obtained. The lining was burned into place when the retort was preheated for furnacing. This lining resisted iron slags but as in the case of the cast carbide units it cracked easily and let the slag attack the retort.

Queneau also worked out a means of making retorts consisting of layers of different materials. The inner layer was of a material resistant to attacks by the change, the outer layer of a material resisting the action of the firing fuel, and the inner layer to form the body of the retort and give it strength. This vessel was unsuccessful because of the tendency of the layers to contract and expand at different rates, causing separation and cracking.

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* American Zinc Co. of Illinois, Monsanto, Ill.

† Phelps Dodge Corporation, Douglas, Arizona.

Controlled Drying of Retorts

By R. R. FURLONG and D. H. WERTZ

DISCUSSION

(*L. P. Davidson presiding*)

A. E. LEE*—I would like to ask Mr. Neale if he has determined the moisture content of his dried retort. Also, has he ever experienced difficulty with bending in the dry room where the green wet retorts contain 17 pct moisture and are placed 3 in. apart?

M. M. NEALE (replying for authors)—I cannot answer your first question as we have had no experience with that. Setting the retorts 3 in. apart, we had no trouble with bending. We thought we would, anticipated we would, but did not.

L. P. DAVIDSON*—You mention,

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* Blackwell Zinc Co., Blackwell, Okla.

* American Zinc Co. of Illinois, Monsanto, Ill.

Mr. Neale, in your opening remarks that some of your colleagues in the zinc industry were somewhat skeptical about the use of it. I can say from second-hand knowledge that about 15 years ago the Hohenlohe people in upper Salesia had some sort of patented scheme basically such as you have done here and as the demand for zinc in 1937 came along they had a number of furnaces down—down for a long time, and did not have an adequate supply of retort to start with. They used in principle the same process that you did and they were using the clay retort Mr. Morgan described. They had very successful drying, cut down their retort inventory tremendously, and they were very well satisfied with it.

Development of Muffle Furnaces for the Production of Zinc Oxide and Zinc at East Chicago, Indiana

By GUNNARD E. JOHNSON

DISCUSSION

(L. P. Davidson presiding)

E. D. HYMAN[*]—How much sorting of scrap is done?

G. E. JOHNSON (author's reply)—We do practically no sorting. We charge "run of mine" scrap to the furnace. The unmeltables, mostly iron, are in such demand today that there is no difficulty in disposing of them. It may soon be desirable to sort out from the unmeltables as much of the brass as possible.

J. J. BRUGMAN[†]—We have somewhat similar problems in the secondary aluminum business. What is your method of removing the unmelted material from the furnaces? Why have you such an apparently small space in which to charge your materials? Do you find that you have to seal that opening, or can you have it open and continuously charge at one end and pull out the other?

G. E. JOHNSON—Our means of melting scrap is efficient only to the extent that we use the waste heat from the vaporizing chamber to do the job. It is a batch process. We open the charge door and place the scrap on the hearth by hand shoveling. The door is then closed during the melting down period. After the melting is complete, the opposite door is opened and the unmeltables are raked out. The doors are approximately $3\frac{1}{2} \times 4\frac{1}{2}$ ft and are not sealed during the process only closed. They are nominally tight. Some metal is oxidized in the process. We have visualized a means of conveying the materials through this melting unit with the metals that are melted trickling out during its travel.

T. H. WELDON[‡]—Mr. Johnson, in line with the last question, is it necessary to seal the furnace between the melting down and the vaporizing unit, or have you got an inverted syphon in the bottom of the chamber?

G. E. JOHNSON—That was one of the first things we encountered. We had to have a sealed opening, and it is a molten metal seal.

You have indirectly asked me another question, which was: "Do you have to seal up the melting unit?" I would say we should exclude as much air as possible, although we are not too efficient in doing that. We allow the melting unit doors to be open when we charge and when we remove unmeltables. You can readily see that that would lead to the idea of having a controlled atmosphere in the melting unit, and I think this would do a more efficient job of melting the scrap.

T. H. WELDON—How often do you charge the furnace?

G. E. JOHNSON—We charge the melting unit, and rake out the unmeltables, about every hour.

H. R. HANLEY[*]—Are any provisions made for controlling the rate of oxidation for the production of various size particles for certain characteristics of the zinc oxide product?

G. E. JOHNSON—Yes, there are many. You are getting pretty much into the fine points of zinc oxide manufacture. Some of us still think we have something to learn about that. In general, this muffle furnace as I have described it to you produces a rounded particle of zinc oxide which is generally formed by a rapid oxidation of the zinc vapor, followed by rapid cooling. We have gone to the other extreme in some of our experiments. We have changed the furnace to produce a type of zinc oxide, such as we thought was peculiar to American process zinc oxide, by controlling the temperature at the point of oxidation and maintaining that temperature for a much longer period of time than we do when we make the rounded shape.

There are other relationships that this furnace readily provides. One of the important factors is the ratio of air to zinc vapors. We can vary that by varying the air supply to the baghouse, or vary the rate at which we are vaporizing the zinc by the simple expedient of regulating the temperature over the carborundum arch. We have a number of variables that permit us to produce all of the grades of French process zinc oxide from lead-free up through the highest grades of seal oxides. There are many controls that we can apply to the operation. What I have said is but a brief condensation.

K. MORGAN[*]—Can Mr. Johnson give us some idea of the fuel consumption of the furnace? How much oil does he use per ton of zinc distilled? I am also interested to know what sort of heat transmission he gets through the arch? What is the thickness of the tiles used to construct the arch? Some time ago we built a small furnace for a different purpose, using a carborundum arch, and we found that the reflectivity of the molten zinc surface was so great we had to use a very high arch temperature. We found we made an improvement by having a layer of carbon on the surface of the zinc. Has Mr. Johnson had any experience on these points? Does he make any sort of insolubles which he leaves in the furnace which he cannot tap out?

G. E. JOHNSON—I believe your first question was the fuel consumption. If I recall, somewhere in this paper there is a test that I quote. I believe we used 800 gal in a given period of time. Offhand I cannot translate that into tons of metal. I might also state that we have this understanding; that the carborundum arch, as the temperature becomes higher, becomes more efficient in heat transmission. As a matter of fact, I believe it is at about 2600°F or higher that the highest efficiency of heat transmission becomes available. We have calculations that I cannot quote from memory which indicate that the carborundum arch does a really very fine job for this type of furnace. Another point that we had considered was the fact that this furnace could be readily constructed so as to furnish an ideal source of heat for waste heat boilers. If a carborundum arch was used over the melting unit, we would have no zinc vapors in the gases at all—just clean combustion gases from which we would have removed some of the heat.

L. P. DAVIDSON[†]—The insolubles?

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[†] Idaho Smelting, Seattle, Wash.
[‡] Consolidated Mining and Smelting Co., Trail, B. C.

[*] Missouri School of Mines and Metallurgy, Rolla, Mo.

[*] Imperial Smelting Corporation, Avonmouth, England.
[†] American Zinc Co. of Illinois, Monsanto, Ill.

G. E. JOHNSON—Insolubles to me means anything that we could not tap out of the furnace. Is that correct? Let us start with the new furnace first to be technically correct. As we charge scrap into any furnace of this type there is, of course, an absorption of metal by the brickwork. That is very small in these furnaces. In fact, our recoveries of zinc over all are better than 98, probably 99 pct, accounted for. As far as I know, except for that furnace absorption and small amount of zinc we use in the molten-metal-seals, it all taps out of the furnace. You may be thinking of another thing on which I have not touched and that is the amount of dross formation in the melting of that scrap in the melting unit. There is a mush which sometimes might get into the vaporizing unit and form the insoluble you were thinking about. We have solved that. I mentioned a trough leading from the melting unit to the vaporizing unit. That trough, just before it enters the sealed opening, widens out to a large bath just outside of the vaporizing unit. If any dross forms, it collects on the surface of the metal at that point, and before it enters the vaporizing unit. We skim it off there in an opening provided in the furnace, and thereby prevent the very large part of the dross from ever getting into the furnace.

L. P. DAVIDSON—That is, in that canal between the melting section and the vaporizing section?

G. E. JOHNSON—Yes.

E. D. HYMAN—My question concerns scrap—also scrap of the type you get from steel company's galvanizing plants. Do you treat such scrap as that commonly called sal-skims?

G. E. JOHNSON—No, we do not, since sal-skims are oxidized, and this furnace is designed primarily for distillation from metallic, zinc-bearing materials. I thought at first you were going to ask me, do we treat galvanizer's dross? We have treated much of that, as previously indicated. In treating galvanizer's dross we have had to tap out a residue metal from the vaporizing unit toward the end of the run. In fact, we have carried the distillation so far that the irony-residue had to be removed by strong arm methods, "muscular metallurgy." We finally came to the conclusion that galvanizer's dross should be treated in a furnace designed for that purpose. This is an interesting subject and I should like to know some of the answers myself.

A. D. TERRELL*—Is there any appreciable amount of blue powder formed in condensing the zinc into metallic zinc?

G. E. JOHNSON—Our figures indicate that less than one half of one percent of the zinc produced over a prolonged period of operation on zinc is formed as blue powder. That rather pleases us when you look at the figures which I have quoted on retorting where blue powder is very much more of a problem than it is on these furnaces. I think the reason is quite self-evident to us; we heat the condenser—we have facilities for heating the condenser before ever allowing the zinc vapors to enter. One detail I did not mention—we have a little outlet at the top of the condenser with a ball on it to relieve any excess pressure.

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* National Zinc Co., Bartlesville, Okla.

El Paso Slag Treatment Plant

By T. J. WOODSIDE

DISCUSSION

(*L. P. Davidson presiding*)

A. E. LEE*—One question of the flue leading to the tube coolers. What gas velocity is maintained to prevent settling of the finely divided fume?

T. J. WOODSIDE (author's reply)—30 fps. Of course some fume settles out, but is immediately carried away by the screw conveyors.

H. R. BIANCO†—How effective are the soot blowers? Do you have to use any hand lancing?

T. J. WOODSIDE—Only one point, which is right at the top of the economizer and which the soot blowers do not reach, we occasionally hand lance. But everywhere else the soot blowers have been very effective and no hand lancing has been done.

L. P. DAVIDSON*—Do you have considerable variation in the lead content of the fume collected if the lead is higher, and is there greater tendency for the fume to stick on the boiler tubes?

T. J. WOODSIDE—There is very little variation in the lead content. From 5 to 7 pct is the widest range variation we have had and we have noticed no difference in the behavior of the fume.

C. R. KUZELL†—Mr. Woodside has been quite generous with data pertaining to metal and fuel economics. I think he stated that the coal consumption of the furnace was $2\frac{1}{10}$ lb for a pound of zinc recovered. I take it that that is the gross coal input to the furnace. I wonder what the net fuel consumption in terms of coal might be after crediting the fuel equivalent of the waste heat steam recovered?

T. J. WOODSIDE—The fuel value of the waste heat steam is approximately 42 pct of the heat input to the furnace. A very large part of the heat, of course, goes out in jacket water—44 pct.

A. D. TERRELL*—I would like to know how much lead is in the deleaded material.

T. J. WOODSIDE—It is a little less than 2 pct now.

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* Blackwell Zinc Co., Blackwell, Okla.
† St. Joseph Lead Co., Herculaneum, Mo.

* American Zinc Co. of Illinois, Monsanto, Ill.
† Phelps Dodge Corporation, Douglas, Arizona.

* National Zinc Co., Bartlesville, Okla.

The Morenci Smelter of Phelps Dodge Corporation at Morenci, Arizona

By L. L. McDANIEL

DISCUSSION

(*A. A. Smith, Jr. presiding*)

A. A. SMITH*—This is a very complete description of one of the country's major copper producing units, and I know that it is of great interest to the copper metallurgists.

P. T. BENSON†—The matter of build-up of magnetite in a reverberatory furnace is probably of primary concern to any copper metallurgist, and I am much interested in Mr. McDaniel's remarks about using silica flux separately from the regular charge to combine with the converter slag iron rapidly and prevent deposition of magnetite.

In the description of the converter flux makeup mixing of barren quartzite with the pit run ore reduced the alumina content and the reason given for that is again to help reduce the formation of magnetite. Have you conducted experiments enough to be able to tell us just where the breaking point in the alumina content of the converter flux is with regard to the formation of magnetite?

L. L. McDANIEL (author's reply)—Probably it is not so much a matter of quantity of alumina as it is the ratio between silica and alumina, although maybe both count. We try to keep a ratio of about 5 or 6 silica to alumina. Our pit ore will run about 3½ to ratio. We change that by adding barren quartzite until we get about the ratio we want. Then we find that if we use that flux alone it is apt to be rather violent. So we add revert material to bring the silica content down to about 65. We can hold around 63 or 65 pct silica with a silica: aluminum ratio of at least 5 to 1 and get fairly good operation.

ALLAN NORRO*—I have been traveling around visiting different smelters and I also used to go to Garfield. They get about 50,000 tons of copper per converter lining and there has not been any trouble with magnetite in the bottom of the reverb. I would like to know why you do not blow magnetite linings in your converters.

L. L. McDANIEL—I think that is a matter of local practice or preference. Garfield has had very wonderful converter life which they get by magnetiting. We have not actually tried magnetiting at Morenci. But probably for the same reason that some other smelters have not, we think it might not be economical to take the time out to blow linings on a converter.

ALLAN NORRO—It just takes 5 hr once a week and this 5 hr is still production. The production will lose about 2 hr a week, and it does not take down your capacity.

L. L. McDANIEL—I repeat we have not yet done any magnetiting at Morenci.

PAUL T. BENSON—We do practice magnetiting at Tacoma but do not get quite the life on converter lining that Garfield does. If we get 25,000 tons we consider that satisfactory. Sometimes we get 30,000 or better. We do not consider that much time is lost in magnetiting because you are blowing matte while making the magnetite lining. Our practice is, after it is completed, to go right ahead and put more matte in and begin blowing slag.

A. C. LOONAM*—I am interested in the fact that you installed multiclones instead of a cottrell. Has this been satisfactory?

L. L. McDANIEL—Our experience with multiclones on converter gases has been quite satisfactory. We have not tried the multiclones on extremely fine particle size, so I cannot give you any information on that; but on converter gases they have been satisfactory.

PAUL T. BENSON—Mr. McDaniel might add something about the multiclone performance at Douglas. I observed that a few years ago and it seemed to be very successful.

L. L. McDANIEL—We installed multiclones on converter gases at Douglas smelter of Phelps Dodge Corporation with about the same results we have had at Morenci. Very satisfactory.

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* American Smelting and Refining Co., Barber, N. J.

† American Smelting and Refining Co., Tacoma, Wash.

* Boliden Mining Co., Sweden.

* Deutsch and Loonam, New York City.

Distillation of Zinc from Copper Base Alloys

By FRANK POLAND

DISCUSSION

(*A. A. Smith Jr. presiding*)

S. ROLLE*—As one who has been privileged to read Mr. Poland's paper before its publication, I wish to express high praise for it and the record which it gives of the work done by the Research and Development Department of Revere Copper and Brass Inc. in developing a satisfactory furnace for the recovery of metallic zinc from secondary metals by distillation. I have also had the opportunity of studying the operation of the furnace when running on scrap brass at the Detroit plant of Revere, and I can therefore say from knowledge gained first-hand that the unit is efficient and economical when used in conjunction with distillation. However, when I read what Mr. Poland has to say in reference to the possibility of using the furnace for melting copper cathodes for the production of oxygen-free and tough-pitch copper shapes, I am constrained to be somewhat skeptical. No doubt the furnace can readily be modified so as to make it possible to melt cathodes, but that is only a part of what is required to produce refinery shapes.

Because of its construction the atmosphere in the furnace is highly reducing and even without protective gases such as nitrogen the copper cathodes which are substantially oxygen-free will not become oxidized—that is, the copper will remain oxygen-free. If then the molten oxygen-free copper is discharged from the furnace in a closed launder and then to a pouring device which is also closed, in other words follow the Scomet process for the production of oxygen-free copper (OFHC), there is no reason why good quality oxygen-free copper cannot be made by substituting the Wilkins-Poland furnace for a Summey or Scomet furnace for the primary melting. But when we come to the production of tough-pitch copper, the matter is not quite so simple. The experience gained at the Ontario Refining Co. plant in Copper Cliff, Ont., Canada, reveals that when they allowed the copper to remain oxygen-free in the arc melting furnace and then convey it to the molds in an open launder in order to pick up the requisite amount of oxygen, it was extremely difficult, if not impossible, to control the oxygen content and to make sound tough-pitch copper castings. Even in the launder there was clear evidence that the copper was gassy by the constant discharge of copper rain; the resulting castings were of poor quality and lacked uniformity. After considerable experimentation the operators at Copper Cliff hit upon the idea of venting the arc-furnace so as to permit the molten copper to pick up oxygen in the furnace. From then on there was little or no difficulty in producing tough-pitch copper of excellent quality.

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* The Scomet Engineering Co., New York City.

It is my belief that in order to produce good quality tough-pitch copper if the Wilkins-Poland furnace is used for melting the cathodes, it will be necessary to oxidize the bath by venting the furnace so as to introduce air. What will happen to a resistor furnace of this type when operating in an oxidizing atmosphere we do not know because it has not been tried; but I should judge it would not be very satisfactory. And if the furnace is not vented and the copper emerges oxygen-free, then the same difficulties will be encountered as when Copper Cliff attempted to produce tough-pitch using the arc furnace.

Mr. L. W. Bahney, Manager of The Scomet Engineering Co., has informed me that he was unable to produce good quality tough-pitch copper wirebars at Carteret, N. J., when he attempted to introduce the proper amount of oxygen in the launder by exposing the moving stream of oxygen-free copper to the air. In other words, he confirmed the results obtained at Copper Cliff even though the melting was done in an induction furnace instead of an arc furnace.

FRANK F. POLAND (author's reply) —I have the impression that Mr. Rolle is inferring that because air had to be vented to Copper Cliff's arc furnace it will be necessary to do the same for all other furnaces. It is my understanding that the metal as it comes from the furnace at Copper Cliff varies from about 0.005 to 0.01 pct oxygen. Can anyone present tell me if I am correct in this?

J. S. SMART*—0.01 ± is the figure that is generally used.

FRANK F. POLAND—I believe there is more than one way to obtain the same end result and Mr. Rolle does not hesitate to say that he believes the resistor furnace could, in conjunction with the proper pouring equipment, produce good sound oxygen free castings. However, he has some doubt as to the successful casting of good commercial tough pitch refinery shapes. We must not lose sight of the fact that the furnaceman has for a long time, and still is, applying his skill in the production of electrolytic copper castings and that the end result we are seeking is to get molten copper in such condition that when it solidifies in any given mold a level or slightly crown set will result. There is no doubt that fundamentally this is accomplished by the release of gas during solidification. However, there has been a lot of discussion as to how the gas got into the metal and what kind of gas it is but the fact that it is a controlled amount liberated during solidification has not been questioned.

At Copper Cliff I believe it is necessary to vent air to the furnace because it is operated with an arc and I feel quite certain they would get into a lot of difficulty with the operation of the furnace itself if this were not done.

Air is 79 pct nitrogen and in my opinion it is questionable if the amount of oxygen introduced in the arc furnace at Copper Cliff is enough in itself to assure uniform flat set. The set there I feel quite sure is controlled by their furnaceman today, as it always has been, that is between the furnace taphole and the molds.

At Perth Amboy, N. J. some years ago we set up a gas plant where desulphurized and dehydrated producer gas was made. This gas was used to pole several 250 ton reverberatory furnace charges to an oxygen free condition. These charges after having been blown to low set by standard procedure were covered with enough charcoal to supply all the carbon needed for reduction plus an excess to cover completely the bath after completion of the deoxidation step. This furnace was equipped with two casting wheels, one casting wire bars and the other vertical cast cakes. The purpose of that experiment was to find out if copper could be made oxygen-free in large quantities. It was done successfully. The oxygen-free metal was cast into wire bars and vertical cast cakes. The set required the minimum of control by the furnaceman and the oxygen in the wire bars and cakes was approximately the same as regularly produced. This experience shows that properly prepared oxygen-free copper can absorb oxygen between the furnace and molds in an amount sufficient to produce commercial electrolytic set wire bars and cakes.

Some years ago at one of the large eastern refineries the casting equipment was such that it was necessary to pole regularly their large reverberatory furnaces down to 0.005 to 0.01 pct oxygen and during this period hundreds of thousands of good commercial set wire bars and cakes were produced. The oxygen content was 0.035 to 0.045 pct in the castings.

During the development of the continuous casting process a small resistor furnace was used to melt approximately 1000 lb of cathode copper per hour while being flushed with nitrogen. This furnace was equipped with a door so that a standard 15-lb ladle sample could be cast from the molten bath. All of these samples were sound and had a commercially good set.

The three examples that I have given and, I believe, the Copper Cliff practice prove that good commercial electrolytic copper can be cast from oxygen free metal that has been flushed with either air (nitrogen plus oxygen), commercial nitrogen or carbon monoxide plus nitrogen provided proper equipment is installed between the taphole and molds for control of the oxygen absorption from the atmosphere.

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Discussion,* Institute of Metals Division

San Francisco Meeting, February 1949

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* TP 2690 E.

On the Structure of Gold-silver-copper Alloys

By J. G. McMULLIN and J. T. NORTON

DISCUSSION

(E. R. Jette and J. R. Long presiding)

E. R. JETTE*—The way this ternary was developed there are two directly determined points on each of the isothermals except the 700° isothermal, where I believe there is only one. How were the end points determined, and what was the basis for it? Whose work formed the basis for the silver copper line?

M. B. BEVER†—At most temperatures the authors determined three points of the isothermal line. For example it can be seen from Fig 3 and 4 how three points for the 600°C contour line were obtained. The authors took two additional points for each temperature from the copper-silver binary diagram contained in Hansen's volume on constitution diagrams. It is correct that the 700°C contour line is based only on one point in the ternary field which was found by a slight extrapolation of Fig 4.

R. I. JAFFEE*—Are the tie lines representing phases in equilibrium parallel to the silver-copper boundary?

M. B. BEVER—Are you asking that as a matter of principle?

R. I. JAFFEE—I assumed that would follow from principle. I wonder if that is in accordance with the authors' ideas too.

M. B. BEVER—I do not believe the authors obtained any information on the tie lines in the two-phase field. Of course, in the limiting case of very low gold contents the tie-lines approach to the silver-copper boundary, but generally in the two-phase field I do not think that the tie-lines have to be parallel to the boundary.

E. R. JETTE—I am quite sure they do not have to be parallel. You cannot tell from this work in which direction they go.

E. A. GULBRANSEN*—Were any pycnometric measurements made to check the lattice parameters of the alloys?

M. B. BEVER—I did not hear anything about such measurements and I think I would have if the authors had done such work.

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E. R. JETTE—The cameras that were used for this work come in three ranges. Do you know whether they use the most precise range or the more convenient middle range?

M. B. BEVER—As I remember it, the authors used a Phragmen No. 3 camera.

E. R. JETTE—That covered the outer range which is the most precise, and it makes me wonder why the results are only considered good to 2/1000 Å. It is capable of doing better than that. Perhaps that is all they needed?

M. B. BEVER—I think that is so. If you recall Fig 2, the essential quantity to be determined was the temperature above which the parameter is constant. That temperature corresponds to the intersection between the inclined and the vertical parts of the left curve in Fig 2. The precision with which this intersection could be determined was not limited by the precision of the lattice constant measurements.

J. G. McMULLIN and J. T. NORTON (authors' reply)—As Dr. Bever stated in his reply to Dr. Jaffee's question, we did not determine the tie-lines between the two phases co-existing phase in the two-phased alloys. Masing and Kloiber[1] show the lines for the 400°C isothermal section. These tie lines run roughly parallel to the Ag-Cu boundary when the compositions are plotted in atomic percent. We know of no reason why the tie lines must lie in this direction except when they approach the Ag-Cu boundary.

In reply to Dr. Jette's question on the cameras, we used an unsymmetrical focussing type camera covering the range of θ values from 45 to 83°. We did not utilize the greatest degree of precision possible with these cameras because our specimens were relatively coarse filings instead of the very fine powders usually required for precision work. We feel that the degree of precision we did obtain was entirely adequate for this project and that the added time necessary to obtain another significant figure in the lattice constant was not justified.

Platinum-tungsten Alloys

By R. I. JAFFEE and H. P. NEILSON

DISCUSSION

(*E. R. Jette and J. R. Long presiding*)

C. S. SIVIL*—The authors are to be congratulated on their excellent work and on the clarity of their paper.

In our opinion the method of preparation of the platinum was perhaps not the best that could have been chosen. The precipitation of platinum by zinc results in a powder that contains not only a comparatively high percentage of zinc, but also a fairly high content of occluded gases. While the final ignition at 750°C would remove some of these gases, there may remain a considerable oxygen content, unless this ignition were carried out in hydrogen. The use of this "black" powder invariably results in swelling during sintering. A platinum powder that is freer from this objectionable swelling is that obtained by the ignition of ammonium chloro-platinate, but even such a powder will give a compact which may swell somewhat, not only when the compact is sintered but also when the compact is worked to wire. In some of our early experiments with powder metallurgy at Baker and Co. we would often make a platinum wire which, on annealing, would swell from a diameter of 0.015 in. to a diameter of 0.017–0.018 in. It is our opinion that this swelling results from (1) the cold welding of the surface of the compact due to the pressure of compacting, and (2) the sintering of this surface to a layer impervious to gas before the temperature of the inside of the compact was high enough to permit diffusion so that the elimination of entrapped gas could not proceed. Some support is given to this view by the observation that the swelling was reduced by reducing the compacting pressure or the cross-section of the compact.

Turning our attention to the micrographs, the writer is inclined to agree with Price, Smithells and Williams that the structures of Fig 9 and 10 are due to sintering in the presence of a liquid phase, despite the argument of the authors. Is it not conceivable that the presintering of these alloys resulted in slugs that consisted mainly of a platinum-rich matrix which, when the slugs were sintered electrically, became liquid before sufficient tungsten had dissolved to raise the melting point above the sintering temperature? Prolongation of the sintering would answer this question. The writer's view would be that the high intersolubility of platinum and tungsten led to the structures observed for the alloys containing 6 pct and less platinum and 38 pct and more platinum; in the tungsten-rich, by rapid diffusion of the molten platinum into the tungsten and, in the platinum-rich, by rapid diffusion of the tungsten into the molten platinum. Perhaps Messrs. Jaffee and Nielsen kept record of the heating curves of their sintering of these alloys and such curves may give an answer to this question.

R. I. JAFFEE (authors' reply)—Mr. Sivil's comments on the swelling of high platinum content alloys are very well taken. In our work in high platinum alloys, swelling during sintering could not be overcome. Consequently, we are glad to have his suggestion on the use of ammonium chloroplatinate ignited in hydrogen to reduce swelling. Concerning the presence of zinc in the platinum powder used, we believe that any present would have volatilized during the high temperature sintering operation. At one time we had occasion to try to make tungsten base alloys containing 10 pct Cr. By the time the bar was sintered, all of the chromium had volatilized. In view of this we believe that zinc would have volatilized also. Our point concerning the so-called "heavy metal structure" still should hold. In the theory of this structure it is assumed that the matrix present in the final product is molten at the sintering temperature, and represents the equilibrium condition. If such were the case it is highly improbable that the bar would support its own weight, which it would have to do during electrical sintering.

S. J. SINDEBAND*—Were any fusion point measurements made on bars which had been completely sintered prior to making this determination? Perhaps that would cast some light on the point just raised regarding the possible presence of liquid phases. I wonder, when the fusion point is measured in the course of the sintering operation, whether the equilibrium is always obtained prior to the initial appearance of fusion in the hole.

R. I. JAFFEE—Perhaps I did not make the point clear, but there were two steps involved. The first step was to prepare the alloy, which involved taking it up to a known sintering temperature. As a second step the specimen was necked down and was taken up to the fusion point. We hoped to attain equilibrium by the first step, the sintering operation, and did not expect any further diffusion during the fusion point determination.

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S. J. SINDEBAND—Perhaps the confusion comes from the text proper, because there is a statement there that the presence of the hole did not interfere with proper sintering.

R. I. JAFFEE—That is right, but the hole was put into the specimen before the sintering operation and before the fusion point determination.

H. P. NIELSEN (authors' reply)—The diffusion takes place very rapidly at the very high temperatures. While we have no complete evidence that perfect diffusion had taken place nevertheless within a matter of minutes the diffusion would have taken place so that it would be practically perfect.

E. R. JETTE*—The melting point or the solidus points seem to be very sensitive to small amounts of impurities, and perhaps the only adequate answer is to report some spectroscopic analysis of your ingots before sintering and after melting to see if there was anything that could affect the melting points.

R. I. JAFFEE—The experiments with tungstens of different nonmetallic contents indicated the extreme sensitivity of the solidus temperature impurities. It has been some time since we did this work, and I do not think the specimens are available to examine spectroscopically. It would be a good idea, however.

E. R. JETTE—We do not often get papers where the working temperatures start over 1700°C.

E. A. GULBRANSEN†—Would you elaborate on the methods used for measuring the temperature? In particular, how is the absolute temperature determined from the brightness temperature?

R. I. JAFFEE—The temperature measured was that at the bottom of a hole in the specimen, which was assumed to be radiating under black body conditions. This temperature was taken to be the true temperature. When I referred to brightness, I was referring to the relative brightness at the bottom of the hole compared to that at the surface of the bar. Perhaps I do not get the entire connotation of your question. Do you care to add anything further, Dr. Nielsen?

H. P. NIELSEN—Only that I understand that the hole should be five times as deep as the diameter or better in order to come close to black body conditions, and we made sure we had at least that depth.

E. R. JETTE—Is there any way of getting an accurate calibration of temperature under these conditions?

R. I. JAFFEE—The method used to measure temperature is admittedly not the most ideal one. A very good method employs the use of a cylindrical specimen with a small hole in it. Under such conditions a practically perfect black body is obtained. If there were no radical temperature gradients through the walls of the cylinder the conditions would be right for very reliable observations of temperature. Use of such a specimen was not feasible in the present work.

E. A. GULBRANSEN—Is it possible to interpret the etching pits as residual porosity of the material?

R. I. JAFFEE—I cannot answer that question absolutely. It is possible that they might be. However, they did not appear in the polished specimen before etching, and, also, were rather shallow.

E. A. GULBRANSEN—Did the density of the material come up to what you would normally expect of compositions of this type?

R. I. JAFFEE—We did not check density.

E. A. GULBRANSEN—How do you interpret your hardness measurements? You have a tremendous increase here, 160 to about 900. To what do you attribute this change?

R. I. JAFFEE—Straight solid solution hardening of the tungsten solid solution by platinum. A similar sort of thing, although not nearly so marked, occurs at the platinum end of the system. Tungsten is one of the most potent of the hardeners of platinum. Although I agree with you that this is a remarkable increase in hardness for a substitutional solid solution, we do not see any other mechanism for the hardening. The maximum point in the hardness curve coincided with the solubility limit.

E. A. GULBRANSEN—Are there any changes in the lattice parameters?

R. I. JAFFEE—Yes, lattice parameters were measured. Some figures are given in the paper. Thus, for pure tungsten we obtained a lattice constant of 3.1583, which checks quite well with the accepted value. A 4 pct platinum content in the tungsten causes the lattice constant to decrease to 3.1572, which amounts to a very small shift.

L. D. JAFFE*—In connection with Mr. Gulbransen's comment, is there any possibility of a precipitation on cooling from the sintering temperatures or with the specimens quenched in some fashion?

R. I. JAFFEE—Cooling from the sintering temperature was quite fast, because after the transformer is shut off, the specimen cools to below a red heat in a few seconds. Therefore the opportunity for precipitation is rather limited.

H. R. STEPHAN†—Is there a possibility that you get a high strength matrix to hold your specimen together and still have a liquid phase present.

R. I. JAFFEE—The micrographs show fairly clearly the matrix was the platinum-rich solid solution. I think that rules out that possibility.

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Use of Electrical Resistance Measurements to Determine the Solidus of the Lead-tin System

By R. HULTGREN and S. A. LEVER

DISCUSSION

(E. R. Jette and J. R. Long presiding)

M. B. BEVER*—The method reported in this interesting paper promises to be of fairly wide applicability. It may be expected that the solidus and liquidus lines in other low-melting alloy systems can also be determined by resistance measurements. As these alloys are especially slow to reach equilibrium, a static method will improve the accuracy with which these parts of their phase diagrams can be determined.

It should be noted that the sensitivity of the method for the determination of the solidus is not the same at all compositions. The straight line representing the solid phase and the curve representing the two-phase region intersect in a decreasingly definite manner, as the temperature range of solidification increases.

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A question must be raised concerning the eutectic temperature in the lead-tin system. The authors state that melting begins at 183°C, but in Fig 5 they somewhat arbitrarily place the eutectic at 185°C and in Fig 6 at 183.3°C. It may well be asked whether the resistometric method is not capable of high precision also in locating the eutectic temperature.

If the resistances of the liquid alloys reported in this paper are plotted against composition at a single temperature such as 320°C the value for the alloy containing 19 pct tin appears to be abnormally low or possibly that for the 24 pct tin alloy is unduly high. Although the authors did not intend to determine absolute values of the resistance, they perhaps have an explanation for this unexpected behavior of the resistance as a function of composition. It is of interest in this connection that Bornemann and Müller* and Matuyama† found that the resistance of liquid lead-tin alloys decreases quite regularly as their tin content is increased.

A recently published observation may be added to the data from the literature presented in Fig 7. Borelius, Larris and Ohlsson* used resistance measurements to determine the solvus in lead-rich lead-tin alloys. They found that an alloy containing 18 pct tin on heating becomes a single phase at 182.5°C, and is still solid at 183.8°C. These data agree well with the results presented in Fig 7 by Professor Hultgren and Mr. Lever.

E. R. POTTER†—It is nice to run across papers where the authors present their data as they record them rather than making their graphs agree with their conclusions. Now in respect to this one alloy—the 19 pct tin—which happens to have a rather low value at some temperature in the liquid state, we do not know whether Dr. Hultgren used the same tube for all his alloys or whether he used various tubes during the experiment. If he had used different tubes, there would be some experimental error due to the cross-sectional area variations from tube to tube. It might be that Dr. Hultgren would have a rather simple answer to this point but I cannot answer the question.

E. R. JETTE—This is one of the oldest systems in physical metallurgy.

B. GONSER*—I might point out that the tin used is not a particularly pure tin, although it is mentioned as such. It is commercial grade. Tin of higher purity can be obtained both in commercial brands guaranteed 99.9 pct pure, and in special grades. I would recommend that similar work be done with tin of higher purity such as the 99.99 pct electrolytic tin produced by Vulcan Detinning Co. or others.

E. R. JETTE—If we are looking for the easiest possible system to try out the electrical resistance method, I would say this would be it. This is not to detract from the work but there is a certain precision attainable in handling this particular system and it would be difficult to reach in a system that melted 500° higher. Also, it is obvious that using the electric resistance method means you must be able to put the alloy in such a physical form that you can measure a resistance. This is not always easy and I suspect that the authors of the previous paper on the platinum-tungsten system might have had a great deal more difficulty in doing the job by resistance methods.

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* K. Bornemann and P. Müller: *Metallurgie* (1910) 7, 396, 730, 755.

† Y. Matuyama: Scient. Repts. Tôhoku Univ. (1927) 16, 447.

* G. Borelius, F. Larris and E. Ohlsson: *Arkiv f. Matematik, Astronomi och Fysik.* (1944) 31A, No. 10.

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The Effect of Orientation Difference on Grain Boundary Energies

By C. G. DUNN and F. LIONETTI

(E. E. Schumacher and A. Wachter presiding)

W. G. BURGERS*—It seems almost certain that this investigation shows the way which finally, when more analogous data have been obtained, must lead to the understanding of many features of preferential growth-directions of crystals and of the occurrence of recrystallization textures.

In this connection I should like to mention that Mr. Tiedema in my laboratory succeeded in developing an analogous method for preparing crystals in aluminum plates with a chosen crystallographic plane and direction parallel to the surface of the plate (to be published in *Cryst. Acta*). If such crystals were grown in high purity aluminum and test-pieces containing a few crystals such as the authors describe were prepared for this metal, it might be possible that due to the absence of growth obstructing particles, even in this low-melting point metal boundary displacements approaching equilibrium positions might be realized.

With regard to the apparently marked drop in surface energy for orientation differences approaching zero degree, and orientation differences approaching those existing between twins, it seems of interest to remark that in aluminum a crystal growing at the expense of fine grained material cannot (or can only very reluctantly) absorb grains in either approximately (within 5–10°) parallel *or* spinel twin orientation (May, Tiedema and Burgers, *Nature* (1948) **162**, 740 and *Cryst. Acta* in press). Consequently with aluminum the method of preparing a crystal with a definite orientation does not succeed when the new crystal has to absorb its own texture; for example it is not possible to grow in a polycrystalline wire with a [111]-texture a crystal with a [111]-direction parallel to the wire axis (Tiedema: *Cryst. Acta*, in press). Finally I should like to mention the well-known fact (Burgers: *Proc.* Acad. Amsterdam (1947) **50**, 723) that prolonged annealing of recrystallized nickel-iron sheet with cube-texture never succeeds in transforming this into one single crystal of the *same* orientation; if, by "secondary recrystallization," large crystals are formed in this process, their orientations differ considerably from the [100]-orientation. In other words, elimination of the boundaries between nearly equivalent blocks appears to be impossible. This again confirms the occurrence of a drop in surface energy for small differences in orientation.

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C. G. DUNN and F. LIONETTI (authors' reply)—The authors wish to thank Dr. Burgers for his kind remarks and his very interesting discussion on the problem of recrystallization and grain growth processes. It is a pleasure to hear of the successful work done in his laboratory on growing aluminum crystals in plate specimens with each crystal having a predetermined orientation. Application of this method to the problem of grain boundary energy measurements in aluminum would be very desirable and, as Dr. Burgers indicates, the purity of the system could be controlled more completely than it can in silicon iron. Results different from our present ones might also be expected because of (1) a different type lattice and (2) a one element system.

The illustrations of lack of growth for near twins and for grains of nearly the same orientation are very welcome and we are in complete agreement with the idea expressed about low boundary energies playing an important role. For example, the presence of relatively stable island grains of near twin orientation, described by Burgers* in connection with samples supplied by P. A. Beck, is understandable on the basis of a low amount of boundary energy for twins or near twins. Further, when island grains form in a growing grain as may occur in exaggerated grain growth, a certain amount of grain boundary energy is lost for purposes of advancing the boundary and this may be important for general growth. Speculating a bit on the assumption that growth occurs, it would seem that the number of island grains would increase with sharpness of texture of the matrix provided the growing grain has about the same or a twinned orientation of the matrix texture. In such a picture not only would the total available energy drop with increasing sharpness of texture, but the amount used for general growth would also drop. From an energy standpoint, these two factors appear to explain the failure of a large grain to grow at the expense of its own texture as Dr. Burgers stated was the case.

However, Dr. Burgers is well aware that something beyond grain boundary energy appears to be involved if we consider the case when the matrix is strained. Quoting from his reference in *Nature*, "It appears from various experiments that the ease with which a crystal can grow in a deformed matrix depends on the mutual orientation of growing and disappearing lattice domain." This idea has been stated before by van Arkel[7] and Barrett[8] and used recently by Dunn[9] and Beck[10] in discussing recrystallization phenomena. We believe from an energy standpoint alone, for instance, that a strained single crystal should be able to recrystallize readily to its own orientation through a nucleation and growth process. However, except for certain recovery processes,[11] which are very slow, recrystallization does not occur except through a change in orientation. A growing nucleus actually must build up a grain boundary energy and the amount of this increases with difference in orientation. Additional knowledge of the nature of the strain energy is needed, of course, for an understanding of this phenomenon even though such energy might be considered to reside as sub-boundary energy and be largely due to differences in orientation.[12,13] Geometry of these subboundaries would be expected to be important. Geometrical relations might even provide the key to this phenomenon of orientation relations being so important to the movement of atoms from one lattice to another. On the other hand, part of the picture may be concerned merely with the rate at which atoms can leave one lattice and join another. This means that, with the same strain energy available, the nature of the boundary where atoms are moving may play a major role.

The importance of the role of orientation relationships for atomic movement also stands out for those cases where boundary energy and internal strain energy both favor the shifting of atoms. An example of this type is the strained island grain (Laue asterism), which appears to be relatively stable in a strain-free single crystal matrix of near twin orientation (see Burgers' report in *Nature* referred to by him).

A. J. SHALER*—My colleagues and I have also been doing some work on the surface energy of solid metals and we wish to assure Dr. Dunn and his collaborator that we fully appreciate the importance of their work. I should like to ask the authors if they have made any measurements of the angles formed at the intersection of the boundary with the free surface at the edges. In general, their edges were notched in the specimens shown, so that these measurements could probably not be made on them. The relation between the angles and the surface energies should be the same at these intersections as at interboundary intersections. The advantage in making such measurements would be that the boundary energy could be directly compared with the surface energy of the metal (itself in the presence of hydrogen or argon). The paper by Udin, Shaler and Wulff which will be presented later shows a method of measuring directly the surface energy of the metal in the presence of its vapor or another gas. From those measurements and the measurements of the angles I am speaking of, we could then get absolute values of the grain-boundary energies.

C. G. DUNN—We observed one thing which has already made some of our next work on this problem much easier—it is the formation of grooves in the surface by thermal etching (reported also by Chalmers, King, and Shuttleworth in England for the case of silver). It seems to offer an ideal way of studying the positions of grain boundaries as well as this relationship between free surface and interboundary energies about which Dr. Shaler asked his question. I think Dr. Shaler is asking about the angle relationships of grooves at either the edge or on the large flat surface. We have measured no groove angles, but others are doing this. Our connection with this problem so far is to supply samples of silicon iron with known orientation relationships between grains. From the surface energy between the atmosphere and the metal and the groove angles, one can obtain the grain boundary energy for a particular grain boundary. If the energy of one grain boundary of our group could be determined in this way, then all our values for silicon iron could be put on an absolute basis. This we hope to do eventually. If the groove is not too near 180°, this technique may have pretty good accuracy. On the other hand if the dip is very shallow and the angle is near 180°, then I think this method would not be very accurate for determining every type of grain boundary.

Using the groove angles—if they can be measured—it should be possible to check the form of curve that we have obtained. To do this, two-grain groups suffice as specimens. You have a fixed orientation relationship for each two-grain group, and you determine γ for each configuration. If the grain boundary energy varies with orientation difference, this will cause the groove angles to vary also. Consequently, the variation of γ with orientation difference could be determined.

L. D. JAFFE—Dr. Dunn, with your techniques it seems it would be possible to control the orientation of the boundaries since they come out at about 90 and 180° angles. In any case you can adjust the orientations of the grains with respect to the boundaries. Are you planning any work in which you will simultaneously control the boundary orientations and the orientations of the grains?

C. G. DUNN—I am glad you asked

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* *Nature* (1948) 162, 740.

* Massachusetts Institute of Technology.

about that. We are attempting to grow two grains from one end of the specimen in such a way that their boundary will be in a given crystallographic orientation. I think we have already succeeded in getting pretty good pseudo twins by this method. We maintain control of this direction pretty well if on subsequent annealing the motion of the boundary stays parallel to this line, otherwise control is lost. You cannot control all grain boundary orientation in three-grain groups because some have to change to establish the equilibrium angles. However, it might be possible to control one boundary fairly well.

The other thing to do is to determine from prior data a configuration that should be fairly close to an equilibrium condition. It should be possible to grow a three-grain group near this configuration in order to obtain equilibrium conditions on a larger scale and perhaps more easily. I do not know whether you had that in mind, but it is a possibility.

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Influence of Composition on the Stress-corrosion Cracking of Some Copper-base Alloys

By D. H. THOMPSON and A. W. TRACY

DISCUSSION

(*A. Wachter presiding*)

E. A. ANDERSON*—At the outset, I note that you are using a humid atmosphere containing ammonia but that you make no reference to the variable of carbon dioxide content. Edmunds in his work in this laboratory found very marked effects on the rate of failure due to variations in carbon dioxide in the environment. This point is, of course, strongly related to the overall corrosion rate problem since the role of the carbon dioxide seems to be to permit the formation of hygrogroscopic salts which give a controlled moisture film on the specimen surface, which in turn seems to support the intergranular penetration more consistently than would otherwise occur.

(2) Your results with various copper binary systems are very striking. It is curious, however, that the time-to-failure minima all occur at percentages of the alloying element which are considerably below the solubility limits as given in the conventional equilibrium diagrams. If your theory regarding the presence of these impurities in some concentration in the grain boundaries is correct, then either the existing diagrams are not accurate in the room temperature region, or there is a difference in solubility in the grain boundaries as compared with the grains. A study along these lines might be very revealing.

(3) The undesirable effect of silicon in copper calls to mind our own observations on the influence of silicon on the stress corrosion cracking resistance of alpha brass. In this case, silicon was found to have a very marked beneficial effect, particularly when a heat treatment capable of producing a grain boundary constituent was used. I should appreciate it if in the discussion of your paper this point should arise, you would attempt to clarify the difference between the copper-silicon binaries and the copper-zinc-silicon ternary alloys.

D. H. THOMPSON and A. W. TRACY (authors' reply)—(1) We have no data on the constancy of the carbon dioxide content of the air used for the test atmosphere but have believed that the normal carbon dioxide content of the air was as constant as could be obtained by using Edmunds' method of removing carbon dioxide from the air and then adding a measured quantity. In any event, the test atmosphere was the same for all specimens in a test run. We agree with Mr. Anderson that the carbon dioxide content is important in the formation of a hygroscopic film on specimens.

(2) We can imagine that there could be a concentration of solute atoms at the grain boundaries which would be so small that present methods would not detect it even if it exceeded the solubility limit of the alloy. There could be somewhat greater solubility at the grain boundaries for an interstitial solute. There is a possibility that phosphorus dissolves in this way but we believe that none of the other solutes studied does. In our present studies we hope to find out something about conditions at the grain boundaries of some of the systems mentioned in the paper.

(3) Mr. Anderson points out that silicon brass, which has had a high temperature heat treatment followed by a quench, is highly resistant to stress-corrosion cracking. Although the test conditions used by Anderson* et al were different from our test conditions, it is noted that the silicon brasses which had not had the special heat treatment were less resistant to stress-corrosion cracking than copper containing approximately equal amounts of silicon.

G. R. GOHN†—Nonferrous metallurgists and particularly, materials engineers, have been accustomed to thinking that copper-base alloys containing more than 85 pct copper were relatively free from spontaneous cracking under the combined effect of prolonged, high stress and corrosive attack. The data presented by the authors indicate that we must now reorient our thinking and consider that, under certain adverse conditions, copper and all copper alloys may be susceptible to stress-corrosion cracking.

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* The New Jersey Zinc Co. (of Pa.), Palmerton, Pa.

* Symposium on Stress-Corrosion Cracking of Metals. (1944). ASTM-AIME, p. 173.

† Bell Telephone Laboratories, Inc.

For many years we have used the mercurous nitrate test as described in A.S.T.M. Designation B154 as a means of determining whether or not the residual stress in a fabricated copper-alloy part such as a rod, a tube or a manufactured piecepart was reduced to a safe level so that stress-corrosion cracking would not occur in service. Now obviously, as pointed out by Dix,* failure in this test is not caused by corrosion and hence the mercurous nitrate test leads to no understanding of stress-corrosion cracking. However, experience has indicated that fabricated parts similar to those which withstood 15 min. immersion in the mercurous nitrate test without failure, seldom failed in service; while those which did crack in the test frequently failed in service unless the residual stresses were reduced by subsequent annealing, or corrosive attack was prevented by the use of an appropriate protective finish. Tests made by Gohn and Arnold* on strip samples indicated that all of the common copper base alloys could be stressed in bending to values approximating the yield strength of the material without failure in the mercurous nitrate test and this finding correlates well with service observations. Only in the case of cylindrical and spherical parts, or screws and studs under high internal or external stresses, were stress-corrosion failures observed either in the laboratory or in service.

The findings of the authors that stress-corrosion will occur in copper and copper alloys stressed at values well below the yield strength when the corrosive agent is an atmosphere containing ammonia, water-vapor, and air is, therefore, of considerable significance and should greatly aid in the study and understanding of the mechanism of stress-corrosion cracking in copper and copper alloys. Their findings do, however, leave unanswered the relation between time-to-failure and service life. It would be interesting to know if the authors are in a position to evaluate their results in terms of expected service life.

D. H. THOMPSON and A. W. TRACY (authors' reply)—The paper describes a series of laboratory experiments designed to study fundamental causes and not intended to predict service failures. The fact that phosphorus-deoxidized copper will crack under specified laboratory conditions does not in the least affect the probability of its cracking in service. Experience shows that the alloy does occasionally crack in service, but the event is rare indeed.

It appears that one of the necessary factors in service failures by stress-corrosion-cracking is that during cold work the alloy acquires a high internal stress, which is not relieved by subsequent creeping or relaxation. Such metal is prime for cracking. In general, phosphorus-deoxidized copper is not capable of maintaining such a residual stress and so it does not fail.

Mr. Gohn's remarks on the mercurous nitrate test cover the subject well. It is a test for the presence of internal stress in some alloys; it is not a research tool for work on stress-corrosion cracking.

H. L. BURGHOFF*—The authors have presented a large amount of data which are a most welcome addition to the available information on stress-corrosion cracking of copper alloys.

I should like to emphasize the point which they have brought out with regard to the rarity of stress-corrosion failures of phosphorus deoxidized copper. This class of material has enjoyed widespread use for many years and has a merited reputation for dependability. The only case of stress-corrosion cracking of copper in service which I definitely recall is that of a soft copper tube of small diameter. This sample was of deoxidized copper containing 0.027 pct phosphorus and had several transverse cracks which originated from the outer surface. These cracks were entirely intercrystalline in nature.

The authors mentioned the low yield point of annealed copper as making impossible the attainment of high internal stresses, thus accounting to a great degree for the scarcity of service failures of the stress-corrosion cracking type. However, such phosphorized copper is used in the cold worked condition for which the yield strength as conventionally defined is a high percentage of the tensile strength. Externally applied stresses can be high without significant deformation of the metal although residual internal stresses would be expected to be low because of the relatively low resistance of copper to stress relaxation. Stress-corrosion cracking of hard phosphorized copper is most certainly a rarity. Its extensive service record indicates great dependability in this respect.

The experiments on the effect of precipitation of iron phosphide in copper as described in the paper and summarized in Table 10 might have been more significant if the authors had used greater amounts of iron than 0.006 pct for the formation of iron phosphide with 0.024 pct phosphorus. As Fe_2P is the most likely combination of iron and phosphorus in copper, approximately 0.09 pct iron would be required to obtain the maximum precipitation effect with 0.024 pct phosphorus.

The test results presented for the copper-silicon series are interesting and worthy of special comment. A minimum of resistance to fracture in the ammonia atmosphere is indicated at about 1 pct silicon and work on a somewhat similar program in our laboratory is in agreement with this. The observation, however, cannot be transferred to prediction of actual service behavior of commercial silicon bronzes without consideration of other factors. For example, two important groups of silicon bronzes have nominal contents of 1.5 and 3 pct silicon respectively and their general service behavior when used as bolts does not at first glance confirm the authors' relationship. This may be due to their being used more in the cold worked state than in the annealed state, with the degree of working normally being greater in the case of the lower silicon content. The 3 pct silicon alloys, while being very serviceable, have shown a number of stress-corrosion cracking failures, whereas such failure of the 1.5 pct silicon alloys seems to be as much a rarity as in the case of copper. As far as laboratory stress-corrosion tests in ammonia atmosphere are concerned, our results on two silicon bronzes containing 1.5 and 3 pct silicon respectively and 1 pct zinc as a third element in each, indicate that the two materials will fracture in approximately the same time at a given applied stress when they are cold worked to the same level of hardness or tensile strength.

The occurrence of transcrystalline stress-corrosion cracks in alloys such as Arsenical Admiralty, as illustrated in the authors' Fig 13, is of importance in the proper diagnosis of service failures by cracking. There was a time not too long ago when transcrystalline cracks penetrating metal from a surface roughened by corrosion were considered direct evidence of corrosion fatigue. Undoubtedly the wrong conclusion has been reached in some instances on the basis of such evidence. It should not be inferred, however, that all cases of stress-corrosion cracking of such materials will be transcrystalline, for intercrystalline cracking may also be encountered in them.

Information on grain size and mechanical properties such as tensile strength and yield strength of the test material was not included in the paper. These factors may not have a great bearing on the trends which were developed, but they may be of significance in a more complete evaluation of stress-corrosion characteristics of these and other materials. It is to be hoped that the authors will tabulate them and add them to the discussion of their paper.

D. H. THOMPSON and A. W. TRACY—Dr. Burghoff points out that the internal stress in cold-worked copper is relieved by stress relaxation and that internal stresses of the order of magnitude of the yield point therefore do not exist. Certainly it is agreed that copper rarely cracks in service. Does not the same mechanism operate in the case of silicon alloys? Our records show that service failures of cold-headed bolts containing 3 pct silicon were ended when a 1½ pct silicon alloy was substituted, paralleling the case Dr. Burghoff cites. We had ascribed this behavior to the ability of the lower silicon alloy to relax and relieve stresses both during cold heading and after installation.

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* Symposium on Stress-Corrosion Cracking of Metals, ASTM-AIME (1944).

* Chase Brass and Copper Co.

The matter of iron and iron plus phosphorus requires additional work. Several heat-treatable alloys have been tested but evidence is generally lacking that precipitation or solution heat-treatments have an appreciable effect on the cracking rate of copper alloys.

The grain sizes and Rockwell hardnesses are given in Table 12. It will be observed that nearly all the grain sizes are between 0.010 and 0.040 mm.

The mechanical properties of the phosphorus alloys are given in Table 13. Samples were annealed for 1 hr at 500°C. The values are averages of two tests.

Table 12 . . . Grain Size and Hardness of Specimens, Final Anneal 1 hour at 500°C

Alloy No.	Alloy Addition Pct	Rockwell Hardness F	Grain Size Mm
Zinc			
8	0.98	35	0.035
10	10.03	51	0.035
11	20.01	60	0.035
12	29.82	64	0.038
14	39.88	74	0.025*
Phosphorus			
4		32	0.040
15	0.001	35	0.035
16	0.002	34	0.040
17	0.004	35	0.030
18	0.007	35	0.020
19	0.014	37	0.030
20	0.028	34	0.035
21	0.056	38	0.025
22	0.10	33	0.030
23	0.24	38	0.045
24	0.46	47	0.040
25	0.93	64	0.018
Arsenic			
4		30	0.040
26	0.052	35	0.025
27	0.126	38	0.020
28	0.19	36	0.025
29	0.305	42	0.020
30	0.36	48	0.028
31	0.607	42	0.020
32	1.22	48	0.020
Antimony			
33	0.010	42	0.025
34	0.109	38	0.025
35	0.25	41	0.025
36	0.47	54	0.020
37	0.95	58	0.015
Silicon			
38	0.11	42	0.030
39	0.27	42	0.030
40	0.46	42	0.030
41	0.98	47	0.020
42	1.97	56	0.018
43	2.96	79	0.015
44	3.92	82	0.015
Nickel			
45	1.98	42	0.040–0.080
46	4.78	47	0.045–0.090
47	9.84	54	0.035*
48	20.16	68	0.030†
49	30.06	81	0.025‡
Aluminum			
50	0.09	35	0.028
51	0.24	40	0.025–0.045
52	0.51	42	0.025
53	1.03	56	0.025
54	1.98	57	0.022

* Alpha grains.
† Final anneal 700°C.
‡ Final anneal 750°C.

Table 13 . . . Mechanical Properties of Copper-phosphorus Alloys

Final Anneal 1 hour at 500°C

Alloy No.	P Pct	Yield Point 0.50 Pct Psi	Tensile Strength Psi	Elongation Pct in 2 In.
5		8,200	34,000	48.5
17	0.004	7,100	33,600	49.0
18	0.007	6,800	33,300	50.0
19	0.014	7,200	34,100	50 0
20	0.028	6,200	33,600	48.0
21	0.056	7,800	35,400	48.0
22	0.10	6,800	35,000	50.0
23	0.24	7,300	36,600	48.0
24	0.46	8,600	39,000	48.0
25	0.93	13,300	43,900	44.0

J. T. KEMP*—The paper by Messrs Thompson and Tracy is the latest in an important series on corrosion cracking. It follows in logical sequence the impressive group of reports presented at the AIME-ASTM symposium in 1944. In reading this paper it is well to look over the volume containing the earlier ones once more.

Two considerations appear to have been overlooked when one reviews these several papers with attention directed to the theory offered: 1. That the path of cracking, whether intergranular or transcrystalline, may be influenced by the structural history of the metal. 2. That the potential relationship, grain boundary to grain body, is probably inconstant, and that the intensity of anodic corrosion at the bottom of a crack may decline as the ohmic resistance of a lengthening circuit builds up.

Now the consensus of opinion regarding corrosion cracks that follow grain boundaries seems to be that such cracks are caused by localized action resulting in one way or another from precipitation or concentration of solute atoms in the grain boundary regions. It seems to be assumed that the susceptible metal was in structural equilibrium at the close of the last previous period of structural change due to the heat, that is, that the grains have been established, that the boundary precipitation or concentration has progressed to a condition approaching stability. Perhaps such conditions may be attained in standard laboratory operations, perhaps not. How certain can we be that more than a semblance of equilibrium has been reached in a recrystallized metal, that solute atoms have migrated from previous positions along previous grain boundaries to new positions along new grain boundaries in sufficient numbers to establish the potentials or the tensions indicated? A very considerable degree of mobility must be assumed to get the solute atoms or precipitates from place to place as new grains form in recrystallizing metal, and then to follow the boundaries as the grains grow. Is it not possible that solute atoms gathered in well established grain boundary regions, assuming that that is where these atoms do congregate, during one interval at annealing temperature may be left more or less in place during cold working and a subsequent interval at temperature, still occupying something of their original planal or zonal positions in the mass and lying across the new grains as much as along the new boundaries? If this were so, it would seem plausible to assume that the residual arrangements of solute atoms, or precipitates, would cause lattice strain within crystals and so offer favorable paths for transcrystalline cracks.

Micrographs of transcrystalline corrosion cracks, however, do not often suggest that the crack follows the polygonal alignment of former grain boundaries very faithfully. Perhaps a residual planar arrangement of residual solute in one crystal at or close to the exposed surface is enough to establish a notch in a stressed metal. The notch effect may predominate once the crack is established. It is not to be expected that the residue of any mesh work of grain boundaries would retain sharp definition through later structural changes. The traces of old boundary systems should disappear as later structures develop. Yet the persistence of coring in the wrought nickel-silvers is an evidence of the persistence of inhomogeneities in alpha copper-base alloys.

As to the electrical circuits and the progress of inter-granular cracks to considerable depth, say through and below the second layer of grains, it may be asked whether microcurrents do or do not obey the general laws governing the flow of macro-currents. Presumably they do. It must be borne in mind that there is an analogy between the flow of current in three dimensional conductors, that is, local currents in a mass of conducting metal, and the flow in restricted circuits that can be measured with precision. Specifically, it would appear that the grain boundary-grain body potential difference could operate only to promote corrosion in a crack to a depth at which the resistance of the lengthening circuit (up through the electrolytic, over the edges to whatever cathodic areas lay adjacent and back through the mass of metal) would reduce the active current to ineffectual values.

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* The American Brass Co., San Francisco, Calif.

A simple anode to cathode circuit may exist only at the inception of a corrosion crack. As soon as appreciable depth was attained there would be modifying potential relationships between the more intensely anodic metal at the bottom of the crack and the less intensely anodic walls until the crack had widened by the removal of enough of the anodic wall metal to reveal cathodic crystal body. When this occurs, if indeed there has been no neutral point at which opposing emf's within the crack stop attack on the walls, the simple anode to cathode circuit can become re-established. Other modifying factors, chemical reactions, polarization, adsorption, and others, may all assert themselves in one or another order or intensity, perhaps inconstantly, to modify the progress of the crack.

Again, cracks that are established by potential differentials may propagate in response to other forces such as stress concentration at the sharp bottom of the notch. In any case, there should be no sharp transition from one to the other regardless of the time rate of progress in any system not subject to fluctuating external influences.

There will be many special cases—perhaps every one observed will be special in some sense—and the wide mouthed crack mentioned above is one.

No potential differences within grains have been reported in our series of corrosion-cracking papers. They would be difficult to identify and measure. Such potential differences are conceivable and have their parallels in other physics. If boundary-to-body potentials exist because of boundary precipitations or concentrations, then a similar potential should exist within a crystal if an interior concentration existed and came through to an exposed surface.

The whole subject becomes more involved the more it is studied. Perhaps the whole has become so wrapped up in words that only a clear sighted prophet can disentangle facts from fancies. May such a one emerge from the laboratories soon and reduce the laws of corrosion cracking to simple language.

D. H. THOMPSON and A. W. TRACY—In the alpha solid solutions of copper alloys, remarks about equilibrium, submicroscopical precipitation, or grain boundary concentration are all pure supposition. Perhaps the observed effects are associated with such causes; as yet proof is lacking.

In some aluminum alloys the conditions can be seen under the microscope. In his 1940 Institute of Metals Lecture,[4] Dix shows a micrograph (Fig 2) in which over-aging of an aluminum alloy containing 1.6 pct copper has resulted in a fine, randomly distributed precipitate that has agglomerated at the grain boundaries and left a solute-depleted zone. As Dix states in the present discussion, either the depleted zone or the precipitate may be the anode that starts stress-corrosion cracking. It is obvious, however, that the atomic movement necessary to form this precipitate and depleted zone is small, and that a solution heat-treatment would readily redissolve the precipitate. Thus, a precipitate can form and be redissolved with only small atomic movements.

In the case of copper alloys there is reason to believe that small amounts of impurities may be swept along ahead of an advancing grain boundary during grain growth. Presumably, this can occur because there is more room, more vacant lattice sites in the discontinuity of the boundary. If this mechanism takes place no precipitation heat treatment is necessary, foreign atoms are concentrated at the grain boundaries by a simple anneal. It is quite possible that the same mechanism explains why some solute atoms inhibit grain growth.

As to the lengthening current path in the deepening crack, an answer can be only conjecture, but certainly this process does not stifle the attack even in the absence of stress. In the presence of stress it has been shown (unpublished work, The American Brass Co.) that the rate of crack propagation is accelerated quite rapidly. Presumably this is the effect of the ever-increasing stress on the notch at the bottom of the crack. Mr. Kemp's idea that the walls of the crack may become cathodic and reduce the length of the current path to the corroding anodic area at the base of the crack is logical. At any rate, it is certain that if the resistance of the circuit increases, that is not the primary factor in determining the rate of crack propagation.

E. H. DIX*—The authors are to be congratulated upon a very nice piece of work which adds tremendously to our knowledge of the subject of stress corrosion cracking. I was a little bit intrigued by the introduction of the paper in which the authors refer to season-cracking of brass as being associated with internal residual stresses and stress corrosion cracking as a proper terminology when the stress is from an externally applied load. I suppose some of us who have been worrying about intergranular corrosion for a good many years do draw a distinction between ordinary intergranular penetration which occurs fairly general along the surface and not too deep in most cases, in comparison with stress corrosion cracking of a material that is susceptible to intergranular corrosion, but where the crack goes through fairly rapidly because of the applied tension stress.

There is reference here to the theory that we proposed some time back, but I think there is more emphasis put on the question of whether or not precipitation occurs than we had intended. In aluminum alloys, especially the aluminum-copper system, I think we have demonstrated pretty conclusively that the anodic condition at the grain boundaries is caused by precipitation. In that case the aluminum-copper compound is precipitated, but it leaves a depleted zone along the grain boundaries which is anodic to the remainder of the grain. In some other systems, in the aluminum alloys the precipitate is anodic. That is particularly true in the aluminum-base magnesium alloys. They are of interest because transgranular as well as intergranular cracking occurs and the transgranular cracking follows slip planes along which there is precipitated constituent. I would like to be permitted to read the conclusion from the paper since I subscribe to it 100 pct, and really it is about all that we tried to put out as a generalized theory:

"Any of these conditions makes the grain boundary region anodic to the grain bodies. Localized corrosion is accelerated and grain boundary penetration ensues. The presence of a tensile stress still further accelerates penetration by opening cracks and forming highly stressed notches."

D. H. THOMPSON and A. W. TRACY—The definitions of season cracking and stress-corrosion cracking are used by the ASTM[8] and The Corrosion Handbook.[2]

Attack in the absence of stress cannot, of course, be called stress-corrosion cracking nor does it have the appearance of cracking. The paper refers to it only as intergranular penetration.

We agree entirely with the quoted conclusion, but we are still eager to find the cause of the shift in potential of the grain boundary in the anodic direction in copper alloys.

The authors are grateful to the several discussers for their valuable contributions to the paper and to the subject itself.

The subject can be summarized by saying that highly localized corrosion cells result from the chemical or metallurgical condition of the metal in a selected environment. Stress accelerates the failure. The paper shows how the composition of the metal may have a large effect on the formation of such cells.

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* Aluminum Co. of America.

Oxide Films Formed on Metals and Binary Alloys. An Electron Diffraction Study

By J. W. HICKMAN

DISCUSSION

(*A. Wachter presiding*)

A. SQUIRE*—I am afraid I missed the explanation of the significance of Fig 3. I do not quite understand what the effect of the thickness of the film is, specifically your interpretation of the effect on the transformation of the oxide, from one type to another. In regard to tungsten copper materials, that is not a true alloy. It is just a mixture of tungsten and copper. Is there a real significance in trying to determine thermodynamic data in a mixture of that sort?

E. A. GULBRANSEN† (*replying for author*)—Fig 3 to which you refer, shows that the Fe_3O_4 to FeO transformation is a function of the oxide thickness. An oxide film of 4000 Å in thickness shows a transformation temperature of 500 to 550°C while an oxide film of 428 Å shows a transformation temperature of 350 to 450°C. The temperature for the thicker film is approaching the normal value of 580°C. We have noted this effect several years ago and have checked the experimental evidence several ways. I would like to interpret this phenomenon as follows: Two equations are involved in the $Fe_3O_4 - FeO$ equilibria.

$$Fe_3O_4 + Fe \rightleftarrows 4\,FeO \quad K_1 \quad [12]$$

$$3FeO + \frac{1}{2}\,O_2 \rightleftarrows Fe_3O_4 \quad K_2 \quad [13]$$

The free energy data for these reactions are well known. The logarithm of the equilibrium constants K_1 and K_2 for the two reactions are given as a function of temperature in Table 6:

Table 6 . . . Equilibrium Constants FeO-Fe_3O_4

t°C	[12] log K_1	[13] log K_2
400	−0.63	17.63
450	−0.43	16.00
500	−0.22	14.56
550	−0.04	13.30
600	+0.09	12.21

Eq 13 is thermodynamically possible even in oxygen pressures found in the best of high vacua at all of the temperatures shown. Eq 12, however, is thermodynamically feasible only below 570–580°C and not above. The temperature dependence of log K_1 is small and even at a temperature of 400°C log K_1 is −0.63. This is equivalent to a free energy change of 1940 calories per mol. At temperatures of 450 and 500°C the energy changes are ⅔ and ⅓ of the value calculated at 400°C. One may say then that the FeO-Fe_3O_4 equilibria is rather unique in the flatness of the free energy curve and that small energy changes associated with thin films of matter may explain the change in transformation temperature.

In regard to the question about the use of tungsten-copper materials, Dr. Hickman mentions on p. 11, of the paper the fact the metals do not form a real binary alloy and that the reactions studied may be indicative of those that obtain with a mechanical mixture of these metals.

S. E. MADDIGAN*—I will have to apologize to Mr. Gulbransen. In discussing the oxide films formed on iron he has pointed out that the transformation temperature for polymorphic transformations within these films seems to depend upon film thickness. His thermodynamic explanation for this is not quite clear to me. Although I have not had an opportunity to check the relative lattice parameters for iron and the oxides in the films, I believe that a suitable explanation can be provided by correlating crystal geometry and thermodynamic potentials. It is well known that for thin films the curves for thermodynamic potential may be displaced if suitable geometric relations exist between the substructure and the material of the deposited film, or in the present instance the chemically formed film. For instance, if one deposits a film of a polymorphic material on a suitable substructure such that the space group of the substructure has a close geometric relationship to that of one phase of the polymorphic material, and if the lattice spacings concerned differ by only 10 to 15 pct, then one finds that the transformation temperature of the polymorphic transition is shifted quite appreciably from that normally found for gross samples of the polymorphic material. I would suggest that something of this nature is occurring in the present instance. In the first thin films mentioned by Dr. Gulbransen, from the thickness one would expect the substructure of the iron to have quite an influence on the overall thermodynamic potential. On the other hand for later thicknesses of the order of 4,000 Å, the forces operating within the volume of the oxide itself assumed the major role and the transformation temperature is then approximately the normal value, so that the film assumes the structure of the normal stable phase.

E. A. GULBRANSEN—I find myself in complete agreement with Dr. Maddigan. My previous remarks were made in order to show that small energy differences could explain the observed phenomena. The lack of matching of the two lattices may account for this difference in energy noted.

R. I. JAFFEE*—I would like to ask if these alloys, particularly those containing chromium and molybdenum and tungsten were analyzed chemically. It seems to me there is a very good possibility of losing a lot of chromium in the preparation from the powders due to the volatilization.

E. A. GULBRANSEN—Dr. Hickman does not say that the alloys have been analyzed chemically. They were prepared at our Bloomfield Lamp Division where many alloys of this type are prepared. The alloys, in both cases, were prepared by slurrying in carbon tetrachloride, the molybdenum or tungsten powder together with the chromium metal powder and also the lubricant. The resulting mixture was dried and pressed into compacts which were subsequently prefired and then sintered in hydrogen atmosphere. According to the ASM Handbook 1948 Edition, both the chromium-molybdenum and the chromium-tungsten systems show a solid solution equilibrium diagram.

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* Battelle Memorial Institute.

R. I. JAFFEE—In connection with the chromium tungsten alloy, we once had occasion to try to make a 10 pct Cr-90 pct W. In an attempt to get the alloy dense it was necessary to sinter at higher and higher temperatures until finally after a dense product was obtained it was found by spectroscopic examination that there was not any chromium left as it had volatilized away. Chromium is very difficult to alloy with a high melting material such as tungsten by straight sintering techniques.

A. SQUIRE—I might be able to shed a little light on that. Dr. Lustman of our Research Laboratories has done some rather extensive work on the preparation of molybdenum-chromium alloys. I believe one of his methods at least was actually to chromize the material, and he obtained molybdenum-chromium alloys in the entire range. On the other hand, I am almost positive that he has obtained a complete series of alloys by mixing chromium powder with molybdenum powder and sintering at a high temperature.

R. I. JAFFEE—I was referring to tungsten-chromium alloys particularly. It is necessary to get the alloy to a much higher temperature with tungsten-chromium, so that the vapor pressure of chromium is appreciably higher than it would be with molybdenum-chromium alloys.

E. A. GULBRANSEN—I have contacted our Bloomfield Works relative to Dr. Jaffee's question. They do not indicate that they had any great difficulty with the volatilization of chromium.

Magnesium-lithium Base Alloys—Preparation, Fabrication, and General Characteristics

By J. H. JACKSON, P. D. FROST, A. C. LOONAM, L. W. EASTWOOD, and C. H. LORIG

DISCUSSION

(L. D. Jaffe presiding)

R. S. BUSK*—I wish first to congratulate the authors of this paper both for the work done and the presentation of that work. We have also been working on this type of alloy development, but any technical contribution I might have is better reserved for a separate paper which is planned in the near future.

However, I would like to insert a word of caution. The alloys described in this paper are still very much in the laboratory stage. There still remains the quite vexing problem of property stability at slightly elevated temperatures which must be solved before the properties quoted can be effectively utilized. These alloys are extremely interesting and I am confident that the problems can be solved. However, the present existence of those problems must not be overlooked.

I have one question with regard to the work-hardening test. If the work hardenability of magnesium is compared to aluminum using a more standard test such as the Meyer Analysis the magnesium is found to work harden the more rapidly. Is the test developed for this work truly a work-hardening test or a measure of something else?

J. H. JACKSON (authors' reply)—I am sure we appreciate the comments of Mr. Busk and we are pleased that the Dow Chemical Co. has also undertaken work in this field. It is a big field. We, of course, are continuing our research for the Navy Bureau of Aeronautics, since, as clearly shown in the paper, the alloys are not completely developed.

With regard to Mr. Busk's comments on the relative work-hardenability of aluminum and magnesium, the comparison we cited in the paper was intended merely to show that the results obtained by our method of testing were independent of the yield strength of the materials. We believe that this test method afforded a rough indication of the work-hardenability of the magnesium-lithium base alloys. It is not known whether this method affords greater or less accuracy than the Meyer Process, which is based upon a hardness-test impression. It is quite possible, since work-hardenability is a function of metal purity, that our results, obtained for commercial aluminum and magnesium, would be different if high-purity metals had been used.

A. C. LOONAM—Lithium has some very interesting effects on magnesium. The paper showed that even small percentages increased ductility. These small amounts changed the axial ratio of the hexagonal magnesium from 1.624 in the pure metal to 1.606 in the saturated alpha solution, a value close to that of titanium, which has a ratio of 1.601. You will recall an article in the January, 1949, issue of the *Journal of Metals* where it was stated that titanium can be cold-rolled over 90 pct without any significant edge cracking. At 4.9 or 5 pct lithium, a change begins in crystal structure—from a hexagonal close packed to body centered cubic. There are two phases over a short range of lithium content, but at 10 pct the structure becomes completely cubic. The melting points of alloys in this range of lithium content are relatively high. Alloys even up to the six ratio have melting points above 500°C; this represents a relatively small reduction in melting point from pure magnesium itself. The magnesium-lithium system has a number of very interesting characteristics. This is only a very small part of the story.

J. H. JACKSON—I would like to remind you that Mr. Loonam is one of the authors of this paper, and the fact is that this work is based on many of his ideas. I am sure we appreciate his additional comments in this discussion.

R. LEITER*—I am interested in Fig 19 in which Mr. Jackson compares strength properties of various alloys after correcting for differences in weight with aluminum as the base. I have been close to the application of stainless steel in light weight structures and this chart appears to me not quite to do justice to stainless steel, particularly in the comparison with 24S-T4 and 75S-T6 aluminum alloy and SAE 1040 steel. For SAE 1040 steel to show up so well it must be in the quenched and drawn condition and the draw must be fairly low. The properties of the aluminum alloys appear to be typical rather than minimum values. The stainless steel properties as shown in the chart are fairly typical of type 301 in ½ hard temper. However, the ¾ hard temper is about the equal of 24ST4 and full hard temper is superior to this aluminum alloy.

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J. H. JACKSON—Mr. Leiter's remarks are well taken especially with regard to the comparison between stainless steel and 24S-T4. Table 11 gives the typical and minimum properties based on the most recent available data.

Table 11 . . . Typical and Minimum Properties

Material	Yield Strength, psi				Tensile Strength, psi			
	Actual		Compared to 24ST on a Strength to Weight Basis		Actual		Compared to 24ST on a Strength to Weight Basis	
	Typical	Minimum	Typical	Minimum	Typical	Minimum	Typical	Minimum
24S-T4 bare	48,000		48,000		68,000		68,000	
24S-T4 clad	42,000		42,000		64,000		64,000	
75ST bare	72,000		73,000		82,000		83,000	
75ST clad	67,000		68,000		76,000		77,000	
Stainless (Type 301) ½H	123,000	110,000	43,000	39,000	165,000	150,000	58,000	53,000
Stainless (Type 301) ¾H	145,000	135,000	51,000	47,000	185,000	175,000	65,000	61,000
Stainless (Type 301) FH	152,000	140,000	53,000	49,000	195,000	185,000	68,000	65,000

The typical property data for stainless steel shown in this tabulation were supplied by Mr. Leiter as being typical of Budd experience. The typical data for the aluminum alloys were obtained from the publications of the Aluminum Co. of America. The data which we used originally in constructing Fig 19 were taken from the National Bureau of Standards Circular No. C147.

The relative properties shown in Fig 19 for SAE 1040 steel were for the quenched and drawn condition, the drawing temperature being about 600°F. The relative properties shown for the stainless steel were for the ½-hard condition. In the ¾-hard condition the relative properties of the stainless steel would be about equal to those of 24S-T4 but inferior to those of 75S-T6.

We wish to point out that the purpose of Fig 19 in the paper was to indicate that the magnesium-lithium alloys are comparable on a strength to weight basis with the aluminum alloy 75ST and superior on this basis to the aluminum alloy 24ST and to stainless steel Type 301

Hydrogen in Aluminum

By Y. DARDEL

DISCUSSION

(L. D. Jaffe and D. W. Smith presiding)

R. EBORALL*—The determination of the hydrogen content of aluminum alloys is of considerable technical value, particularly in the study of casting and welding processes, and any reliable method for its determination is to be welcomed, particularly if it is simple in operation and utilizes techniques which are available in any laboratory.

Modern vacuum hot extraction methods have proved very suitable for the determination of hydrogen in aluminum,[21,22] and not only are highly reproducible results obtained by any one laboratory but there is quite good agreement between different laboratories using very different conditions of extraction.[23] Success depends upon good vacuum technique and upon extreme care in the preparation of the surface. It is standard practice to use a surface turned without lubricant—although other methods, if standardized, may be perfectly satisfactory—and to avoid touching the surface by hand at all. Under these conditions the contribution of the surface to the quantity of hydrogen obtained is constant for all practical purposes. As an illustration of this constancy, and of the reproducibility of the method generally, it may be stated that in these laboratories duplicate hydrogen determinations, even on material as thin as 0.125 in., for which the surface correction is about 0.08 cm^3 per 100 g, generally agree within 0.01 cm^3 per 100 g. Ordinary commercial wrought materials in this country commonly run from 0.2 to 0.5 cm^3 per 100 g of hydrogen, except for high magnesium alloys which may contain rather more, so that for ordinary hydrogen determinations the method has more than adequate accuracy.

I have made this point about accuracy at some length, because Mr. Dardel emphasizes rather strongly the errors to which the work of Ransley and myself may have been subject from variations in "surface" gas. Nevertheless, we did not claim any particular accuracy for the determinations of solid solubility, which were of a preliminary kind and a very small part of an extensive program. In fact we said: "The results do little more than indicate the order of magnitude of the solubility, since it is so small that the errors inherent in the method become serious."* Now that a series of accurate determinations has been made by Ransley and Neufeld,[24] there seems no reason to be dissatisfied with our earlier preliminary results.

The validity of the hydrogen contents determined by vacuum extraction receives confirmation, if any is needed, from observations obtained with a simple method for estimating hydrogen in solid wrought metal, which has been developed by my colleague A. J. Swain.[25]

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[21] References not in the paper are at the end of discussion.

* The method referred to consisted of holding specimens in hydrogen without prior degassing, and subsequently measuring the hydrogen content. The greatest single potential source of error, in the light of later experience, was probably the formation of voids due to some of the hydrogen originally present coming out of solution at inclusions.

The principle of this method, which should be applicable to most of the aluminum engineering alloys, is to heat a thin piece of the metal for a short time in a dichromate bath at a temperature about midway between solidus and liquidus. Blisters are formed, the volume of which is a measure of the hydrogen content. It turns out that the pressure in the blisters, calculated from the known gas contents of the materials used for calibration, is about 1.1 atm. at the test temperature. The hydrogen can thus be converted into blisters which anyone can see for himself. The same sort of thing happens in castings;[24,26] one can measure the density and find the "percentage voids" and one can measure the hydrogen content: on the average, for sand castings, a pressure between 1 and 2 atm. in the voids is obtained.

In the discussion, contained in his penultimate section, Dardel states that the values found by methods other than his own, including the vacuum hot extraction method, are greater than those which correspond to the solubility (in the solid at the melting point and at atmospheric pressure). That is commonly so. He concludes that the bulk of the hydrogen extracted therefore necessarily comes from the surface layers. That is nonsense. Some of it does of course—for our own technique we have measured the quantity and allow for it. But in a casting gas may be present in pinholes as well as in solid solution. In wrought metal it may be present in solid solution at "internal pressures" far greater than atmospheric: the metal can, and frequently does, absorb hydrogen in the solid state by the reaction with water vapor,[21] which has ample energy,[27] and, moreover, the hydrogen present in pinholes in a gassy casting may be forced into solution during hot working. There are no doubt other ways in which extra hydrogen can be accommodated.

Dardel quotes Kljatschko and others to the effect that the metal is riddled by channels, increasing its surface area, and that gas is obtained from this extra surface. I thought we had disposed of this point successfully,[28] and do not wish to go over the same ground again. Klyachko's ideas are contrary to classical gas-metal theory and are based upon his colloidal or micellar theory of metals which is incompatible with the generally accepted one (that is, according to Klyachko's theory a metal is not truly crystalline). Tamman and Bredemeier's results, adduced in support of Klyachko, are very extraordinary; if one is to believe them, any metal is permeable throughout to large dye molecules. Since sound metals including aluminum have no detectable permeability to inert gases including helium,[29,30,31] I suggest that the results need not be taken too seriously. Of course, if the metal contains continuous shrinkage porosity, or severe lamination owing to cold shutting, bad extrusion practice or the like, that is a different matter.

Incidentally the author misrepresents Ransley and myself[21] when he heads his Table 1 "Amount of Adsorbed and Dissolved Hydrogen," and continues throughout to write of "adsorbed hydrogen"[22] when referring to our work. It is true that alumina formed at low temperatures is highly adsorptive, and it may be that the alumina surface film contains adsorbed hydrogen which is subsequently extracted, but we would prefer to think (and in this we agree with Klyachko) that the "surface hydrogen" is produced on heating the specimen, by the reaction of adsorbed water with the metal.

Mr. Dardel's method for determining hydrogen contents is of great ingenuity, and has the advantage that the apparatus is extremely simple. It is not however an absolute method, since it depends in the first instance upon the solubility of hydrogen in the liquid metal, which must be determined by some other method. For this, a number of published results have been averaged. In Fig 1 of the paper, representing some of the data available, the scatter is not very obvious; however, actual results at just above the melting point of aluminum are highly discordant. At 700°C they range from 0.08 cm^3 per 100 g (Röntgen and Braun) to 0.95 cm^3 per 100 g (Baukloh and Oesterlen); there is thus an uncertainty represented by a factor of 12, and this must be reflected in the values for hydrogen content obtained by Dardel's method. If the results of the more recent and very careful liquid solubility determinations of Ransley and Neufeld be accepted, the highest of these figures is correct and the equation used by the author yields results over three times too low.

If the results reported in the paper are multiplied by three, they accord quite well with experience. Thus in Table 4, giving the amounts of dissolved hydrogen after casting, alloys *A* and *B*, which were directionally solidified but from gassy melts, would have hydrogen contents of 0.19 and 0.16 cm^3 per 100 g respectively, whereas *C*, which contains gas porosity, would have 0.38 cm^3 per 100 g. These figures are entirely reasonable.

It seems rash to assume, however, that the hydrogen contents of alloys *A* and *B* are equal to the solid solubility. There may be slight supersaturation during solidification, and bubbles of gas may be trapped by the advancing crystals; only if these effects could be proved absent could the figures be accepted as representing the solid solubility. However, to return from the results to the method itself, there is a limit above which it is impossible to measure the hydrogen content of solid metal by this method; for if the hydrogen content exceeds the solubility in the liquid at the melting point, and if Mr. Dardel's assumptions are correct, the excess will boil off during melting before the pressure reading is taken. This may not be a very serious limitation in practice, however, since such high figures (over approximately 0.69 cm^3 per 100 g[24] are seldom encountered.

There are also further difficulties. One concerns the nucleation of a bubble. The author attempts to show that there is no nucleation difficulty; this may be true in some instances, but the experiments reported on 99.99 pct aluminum suggest that it is not always so. We do know that, in melts of commercial alloys, primary particles of one kind or another are generally present at temperatures well above the melting point; it has been possible to concentrate them with a centrifuge so that they are readily visible under the microscope.[32] With high purity alloys, or even, it may be, with ordinary alloys without certain additions or impurities, these particles may not be present, and nucleation may accordingly present an obstacle to the formation of bubbles.

Another possible source of error is the possible gain or loss of hydrogen from the surface, before the pressure reading is taken. The author assumes that the metal is protected by an impermeable alumina film. That may well be true for many alloys, but no check appears to have been made on it. For some alloys, however, particularly those with high magnesium, the assumption appears of very doubtful validity, since a magnesia film may be formed and this is not likely to have a protective effect.

In short, I think this is an interesting and potentially valuable method, but that not the slightest reliance can be placed on the figures so far reported.

I should like to see the method thoroughly tried out by making a series of estimations, but using the latest liquid solubility data,[31] and comparing the results with those obtained on the same materials by vacuum extraction. If this is not feasible, a more direct evaluation of the possible sources of error should be made.

There is great scope for a really good method of estimating rapidly the hydrogen content of molten aluminum alloys, for foundry control purposes. The ordinary Straub-Pfeiffer reduced pressure test (the author's "vacuum sample") with the 1 mm or the pressure normally used, is as the author points out, very much too sensitive for practical purposes. For a good many years we have used this test in these laboratories with a pressure of 20–60 mm of mercury, for aluminum and magnesium base alloys; actually we recommended the use of such pressures in a report issued to our member firms in 1941. At this pressure the test gives a very useful rough measure of the hydrogen content of the melt, but does not give a quantitative result (unless density measurements are subsequently made). Dardel's method on the other hand, provided it can be established on a sound basis, is ideal for this kind of purpose. It is simple, rapid and gives a quantitative result. The apparatus, like that for the reduced pressure test, could be made robust and easily portable, so that it could be moved around a large foundry to furnaces or casting machines, to take samples at any stage in the melting and casting process and give the answer on the spot. But that answer needs to be the correct one.

M. B. BEVER*—The author finds by the method described in this paper that solid aluminum just under the melting point dissolves 0.058 cc of hydrogen in 100 g of metal. Recently Ransley and Neufeld[24] published solubility data for hydrogen and aluminum that were measured by a very careful equilibrium method. These authors found a hydrogen solubility of 0.036 cc in 100 g of aluminum just below its melting point.

In place of an exhaustive critical evaluation of the method described in this paper, attention will be called only to two major factors. These factors seem of such an important nature as to transcend any conclusions drawn from a statistical analysis of the experimental results. In this connection it should be emphasized that the two factors to be discussed oppose each other and under favorable conditions may partly cancel out in the resulting value of the hydrogen content.

In the first place, a marked weakness of the method is its inability to distinguish between different gases since the assumption that aluminum evolves only hydrogen is probably less well founded than the author believes. Secondly, it is inescapable that surface tension inhibits the formation of gas bubbles as Brower and Larsen[33] have shown quantitatively for the evolution of carbon monoxide from liquid steel. The presence of nuclei reduces the inhibiting effect of surface tension but does so in an unpredictable manner which cannot be reproducible under all possible conditions. In view of uncertainties such as these it seems that results obtained by the method suggested in this paper do not lend themselves to a rigorous analysis.

C. E. RANSLEY† and N. D. G. MOUNTFORD†—We have read this paper and also Dardel's previous one,[19] with some care, since the subject is one with which we are closely concerned. The method he suggests for the measurement of the hydrogen content of aluminum and aluminum alloys is simple in concept, and if capable of giving reproducible and accurate results would have attractive possibilities for foundry control work. Since the publication of this paper therefore, we have constructed an apparatus similar to that described by Dardel and have carried out some experiments to determine what relation exists between the true hydrogen content of a bath of molten metal and the value predicted by the author's bubble-pressure method. The results we have obtained are of some interest, and we would like to take this opportunity of presenting them. We may say now that we believe that the method proposed by the author is open to some criticism on fundamental grounds, and that our experiments demonstrate this. However, we have admittedly carried out only a limited number of tests, and we would welcome any comment Mr. Dardel has to make on our interpretation of them.

Before giving these results, there is one point we would like to emphasize. The method is based upon the assumption that the first bubble is formed in the liquid metal when the external pressure is reduced until it is equal to, or perhaps a little less than, the "internal pressure" of hydrogen in the melt. The value predicted for the gas-content will thus be a direct function of the value of the solubility of hydrogen in the metal at the temperature of test. The author has taken the mean value of solubility from the early published data (ignoring, however, the results of Baukloh and Oesterlen[3] and Baukloh and Redjali[13]) and has derived his equations and constructed his nomograms on the assumption that these data are reliable. They are, in fact, considerably in error, particularly at the lower temperatures, which are the most important from the practical point of view. In these Laboratories we have recently[24] remeasured the solubility of hydrogen in liquid aluminum by an orthodox procedure and have established values which are considerably higher than those previously accepted; since the publication of our paper we have confirmed these values by an independent method, details of which we hope to publish shortly. We find that the solubility at 700°C, for example, is 0.92 cc per 100 g, whereas the value assumed by the author for this temperature is only 0.27 cc per 100 g. In other words, the values of gas-content calculated by Mr. Dardel (assuming that the deduction is otherwise valid) are wrong by a factor of more than 3. It is quite obvious, indeed, that the gas contents he quotes, that is, those given for duralumin, in his first paper, are far too low, since they are much less than the values obtained by hot-extraction measurements; the latter are now established on a firm basis and yield results in good arithmetic agreement with porosity values. We do not want to stress this point any further in the present contribution, since we have already dealt with it in the discussion of our recent paper.[24] We would like to make it clear, however, that we consider the values of solid solubility deduced by Mr. Dardel to be quite without significance. It is true that they are of the right order, but that is due entirely to a fortuitous combination of circumstances.

The bubble-pressure apparatus we have constructed is very similar to that described in the paper. The vacuum chamber is exhausted by means of a rotary oil pump and the pumping line arranged so that the pressure can be reduced at a reproducible speed, that is, to 380 mm in 15 sec and to a limiting pressure of about 5 mm in 80 sec. The temperature of the metal sample is measured by means of a thermocouple inserted into a re-entrant tube in the base of the cast-iron crucible; we have kept this at about 700°C in all the tests we have so far carried out.

We used 30 lb charges of metal melted in a gas furnace for our experiments. When commencing a bubble-pressure test, a sample of the melt was taken in a small ladle and some metal poured into the crucible in the apparatus, which was preheated to the appropriate temperature; the remainder of the metal in the ladle was then cast into a chill mold to form a sample suitable for subsequent measurement of the gas-content by hot-extraction. Two commercial grades of aluminum, 99.2 and 99.8 pct, have been investigated and the results of the various measurements are summarized in Fig 9 and 10. In these figures we have plotted the true gas contents, as determined on the chill-cast samples, against the values predicted by the bubble-pressure measurements. The predicted hydrogen content m (cc per 100 g) has been calculated from the pressure observations on the assumption that it is given by the following equation derived for our own solubility results:

$$\log_{10} m = \frac{-2760}{T} + 1.356 + \frac{1}{2} \log P_{H_2} \quad [12]$$

where P_{H_2} is the "internal pressure" of hydrogen in the melt, which is assumed to be identical with the pressure at which the first bubble is observed.

It will be seen that the results on the 99.8 pct purity metal (Fig 9) are very widely scattered and, in fact, in 4 out of 8 experiments no visible bubble had formed at the limiting pressure of the apparatus (5 mm mercury) although the hydrogen content of the samples varied from 0.16 to 0.63 cc per 100 g. The bubble formation in this alloy was obviously very irregular and the measurement worthless as a measure of gas content. This is, however, perhaps not unexpected in view of the experience of the author with 99.99 pct purity metal, and his general observation that the accuracy of the method decreases as the metal purity increases.

The results on the 99.2 pct purity metal (Fig 10) are of some interest. Unfortunately the melts used for our experiments with this metal had only a limited range of gas contents (about 0.25 to 0.45 cc per 100 g with one exception)

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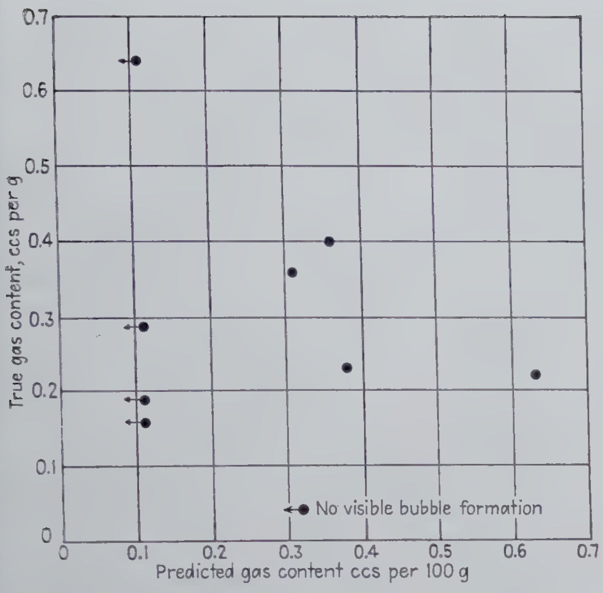

FIG 9—True gas content vs. predicted gas content. 99.8 aluminum.

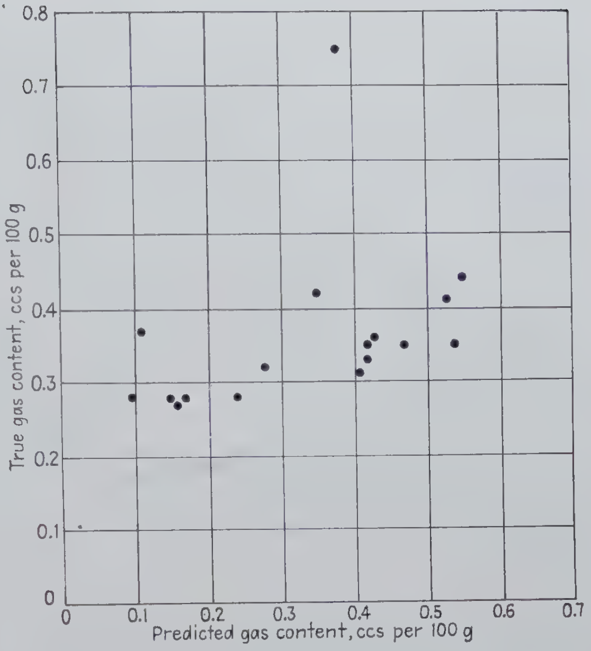

FIG 10—True gas content vs. predicted gas content. 99.2 aluminum.

and it is therefore difficult to draw any firm conclusions from the data obtained. It will be seen that in this case the bubble formation is not entirely random. If the one "rogue" point is ignored, there is statistically a significant correlation between the predicted gas content and the true gas content; in fact, knowing the relationship given by this curve, the true gas content of a melt could be predicted with a standard deviation of about ±0.04 cc per 100 g, but this only holds over such a restricted range of true gas content that the measurement is of little value. The calibration curve is very flat, and in addition, the data plotted in Fig 10 suggest that no formation of bubbles can take place unless the gas content of the metal is greater than about 0.26 cc per 100 g. Further work would be necessary to confirm this, however, and we have not had time to carry out the necessary experiments.

It seems probable that the predicted gas—true gas relationship in the case of alloys such as duralumin will be of the same type as that shown in Fig 10. If so, it becomes possible to understand degassing curves of the type which the author has presented, such as that given, for example, in Fig 2 of his earlier paper,[19] which purports to show a sevenfold decrease in the gas content of a duralumin-type alloy held in an electric furnace for 2 hr. If the values on this curve are corrected to a proper solubility basis, and then converted to true hydrogen contents with the aid of Fig 10 the decrease in gas content on standing then becomes from 0.31 to 0.27 cc per 100 g instead of from 0.07 to 0.01 cc per 100 g. Although this derivation involves several assumptions of uncertain validity, the result is very much of the order that one would predict from practical experience.

We do not propose to attempt a full explanation of the results we have given here. It seems very probable that the relationship between the gas content as predicted by bubble formation and the true value is very much influenced by the experimental conditions. For example, the loss of gas from the sample by diffusion during evacuation will obviously be a function of the rate of reduction of pressure. A fast rate of pumping is therefore desirable from this point of view. On the other hand, if the diffusion of hydrogen to a given point is a rate-determining factor in bubble-formation, a fairly slow rate of pressure reduction would be indicated. Mr. Dardel gives no information as to the rate used in his apparatus and we are unable to say how our conditions compare with his; we should be interested to have some details on this point. From the results of our tests, however, we conclude that although bubble formation is, as one would expect, influenced by the amount of hydrogen dissolved in the metal, there is another factor involved which makes it impossible to apply the simple theory proposed by the author. This factor is, we believe, primarily a question of the stability and surfacing of the gas nuclei which must pre-exist in the melt if bubble formation is to take place at all, and which a simple calculation shows must be of quite appreciable radius. The nature of these nuclei is not known with certainty, but they may well originate from particles of hydrated oxide, which enter the metal mainly from scrap additions. It is of some significance in this connection that in high-purity melts, which are likely to be entirely of virgin ingot material, bubbles are formed only with considerable difficulty. The author has noted this effect in his paper but has not attempted any explanation as to its cause. But whatever the correct explanation may be, it seems clear that a complication exists which makes the proposed method of measuring gas contents of little value as a quantitative tool.

H. UDIN*—There is apparently a misprint in the paper on p. 5, bottom of the first column. This equation should read

$$4702\ (dT/T^2) = 2.5 \text{ pct}$$

The method of determining solubility of a gas in solid metal by measuring the internal gas pressure in the remelted ingot is a very ingenious one. However, the assumption that the surface tension in the nucleating bubble can be neglected because it does not influence the scatter of the experimental results is not necessarily a valid one for several reasons. In the first place, it would be true only if there are relatively few artificial nuclei of widely different sizes present in the melt. However, experiments on undercooling indicate that this is not the case, particularly in metals which have not been especially treated to eliminate centers of nucleation.

If a batch of metal contains n artificial nuclei per unit volume (on the average), then, in measuring any phenomenon dependent on the size distribution of these nuclei, statistical theory indicates that, if the experiment is conducted on a unit volume, there will be a probable error of $1/\sqrt{n}$. If we have as few as one potential nucleus per cubic millimeter, n will equal 35,000 for a 100 g sample, and the probable error is 0.5 pct. This amount of scatter would hardly be noticeable in the 5 pct scatter due to other factors. The surface tension term in the author's Eq 2 can thus have a real effect on the pressure without appreciably influencing the scatter of the experimental results.

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* Massachusetts Institute of Technology.

We can also question the validity of the hypothesis of Eq 3 by drawing on well-known nucleation theory. The minimum size of nucleus which can grow into a bubble is determined by the balance of surface tension with the difference between external pressure and activity of the dissolved hydrogen. Relatively large nuclei may already be present as cavities on the surfaces of solid impurities. If the largest artificial nucleus is of the same order of size as the smallest stable nucleus in every experiment, little dispersion will be found in the determinations, but the error in the basic hypothesis behind Eq 3 may still be large.

Excessive pumping speed may also play a role in minimizing the dispersion of the results. Under these conditions the rate at which a bubble will grow to visible size under a favorable pressure differential would then be determined by the diffusion rate of hydrogen in aluminum as well as by the magnitude of the pressure drop. The difference in the times required for a bubble to grow to observable size from nuclei of even considerable size difference is undoubtedly small, since the volumes of the nuclei are negligible compared with the volumes of the observed bubbles. In this case the surface tension term can again effect the final answer without introducing any experimental dispersion.

Would Mr. Dardel please inform us as to whether his pumping speeds are low enough to permit an equilibrium bubble size to exist at all times?

Mr. Dardel also implies that the surface of the melt is covered by a film which is impervious to hydrogen loss by diffusion. Would he please tell us on what evidence he bases this opinion.

The author's technique may well prove to be of benefit to students of gases in metals. It is therefore of considerable importance that these theoretical questions be cleared up.

F. N. RHINES*—In connection with what has just been said, I think perhaps it is worthwhile to point out that all of the various methods that have been used for determining hydrogen in aluminum failed to take into account one imponderable which is the amount of hydrogen, perhaps combined as water, perhaps as hydrogen, which very likely exists in the oxide film. The critical experiment, it seems to me, that should be run by someone is to compare the apparent solubility by any one method for samples of varying ratios of volume to surface area, so as to find out whether there is a real effect of moisture dissolved in the oxide film. We know, of course, that aluminum oxide is very efficient in capturing water vapor. It is my recollection that the method used by Ransley did not entirely eliminate the possibility of such contamination. Certainly in this case, it seems that some contamination of the oxide film is quite possible. Whether or not hydrogen from that source could turn up in the final analysis is still another question, but I think it needs to be proved one way or the other whether the oxide film can contribute to the apparent analysis.

E. A. GULBRANSEN*—I think one has to consider certain chemical reactions as sources of gases in aluminum. Let us consider the reaction of aluminum with water vapor from the vacuum system to form the oxide and hydrogen. This reaction is possible from thermodynamic considerations and the necessary water vapor is present if the degassing experiments are carried out in the vacuum of a rotary pump.

There are other reactions of this same type forming other gases. I feel that in discussing the liberation of hydrogen and other gases from metals one must consider the fact that certain chemical reactions may occur on the surface forming new gases.

Y. DARDEL (author's reply)—I should like to express my thanks to all contributors to the discussion on this paper for their interest and the care with which they have examined the results described.

Reply to Messrs. Ransley and Mountford:

The first point discussed by Messrs. Ransley and Mountford is of course the solubility of hydrogen in liquid aluminum. At the time of the experiments reported in the paper, the values of Röntgen and Braun, Röntgen and Möller, Bircumshaw as well as Winterhagen, were considered as the most reliable, for they gave approximately the same mean solubility, while the values of Baukloh and Oesterlen were far higher and those of Baukloh and Redjali intermediate. But the determination apparatus suggested being one of relative and not of absolute character the establishment of new and more accurate calibration curves can only be welcome. Therefore as the last measurements of Messrs. Ransley and Neufeld[24] confirm the values given formerly by Baukloh and Oesterlen it might be better to adopt these new values. However, before taking up this step it must be noted that the two sets of data (Röntgen and collaborators as well as Bircumshaw on one side, Baukloh and Oesterlen as well as Messrs. Ransley and Neufeld on the other) do not agree very well with the Borelius' law,[34] while intermediate values do (Fig 11). Of course the Borelius' law is only an empirical one and any departure from it may be observed, but these differences should be pointed out.

The value of the solid solubility given in the paper depends of course upon the value adopted for the liquid solubility. When the solubility at melting temperature in liquid metal is equal to 0.17 cm^3 per 100 g, the solubility at the same temperature, but in solid metal, is equal to 0.058 cm^3 per 100 g. On the other hand, when the datum of 0.69 given by Messrs. Ransley and Neufeld is to be accepted the values of this paper give then 0.15–0.20 cm^3 per 100 g in solid metal. Besides, there may be a slight supersaturation as pointed out by Mr. Eborall and the values given might be a little too high. But if the liquid solubility at melting point is as high as 0.69 cm^3 per 100 g a solid solubility of only 0.036 seems rather low as can be shown from the value of the solubility ratio (Table 8 and Fig 11).

The solubility ratio $\frac{\text{liquid solubility}}{\text{solid solubility}}$ increases with the decrease in solid solubility at melting point, but it does not seem that the decrease occurs as quickly as pointed out by the datum of 19.

During the experiments reported here, the exact pumping speed has not been measured, but as all the authors who have contributed to this discussion have rightfully pointed out its importance, I shall explain at length the method used to choose the proper one.

The pressure is read at the moment given by the observer of the sample surface. The time elapsing between the observation of the bubble formation and the time of pressure reading (or dead time) must be of course so much the shorter as the speed of pressure diminution is higher. When the variation of pumping speed is rapid in the medium pressure range ($1 < p < 150$ mmHg) where the measures are usually carried out, the values read at the higher pressure (and therefore with the higher speed of pumping) can be quite different from the actual ones corresponding to the time of bubble formation, while the measures made at lower pressure (and therefore with the lower speed of pumping) may scarcely differ from the actual one. The computation of such results can only lead to misinterpretation.

At the beginning of the experiments (preliminary experiments not reported in the paper), a one stage rotary pump without the gap *G* (Fig 3) was used; the variation of the speed of pumping varied rapidly with the pressure in the range of pressure measurements and the determinations were wrong.

For instance an Alpax (13 pct Si) was held at 750°C and its hydrogen content was determined at different temperatures between 750 and 580°C. In that way it was possible to vary the formation pressure of the bubble for a given amount

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* Carnegie Institute of Technology.

* Westinghouse Research Laboratories.

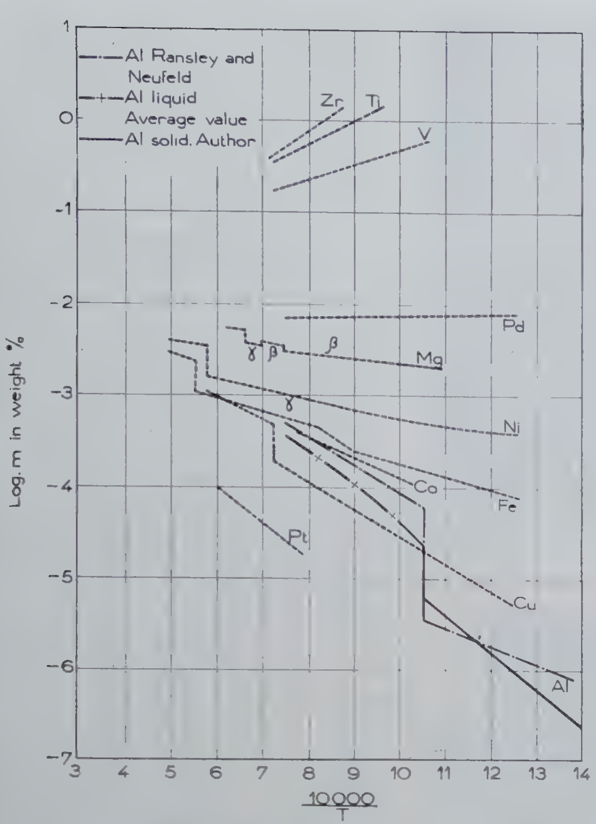

FIG 11—The solubility of hydrogen in different metals.

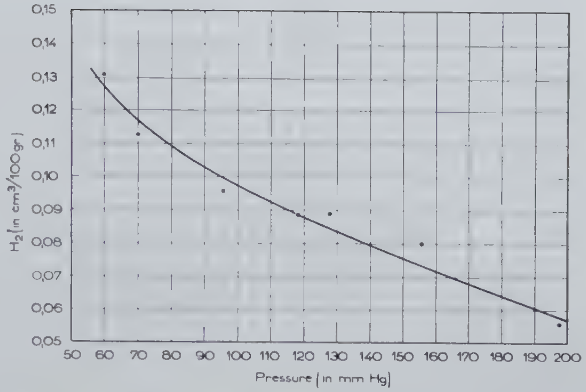

FIG 12—Variation in the determined hydrogen content, when the conditions of pumping are wrongly regulated.

of hydrogen, the formation pressure being so much higher as the temperature was lower.

The results are given in Fig 12. The measured hydrogen content seemed so much lower as the pressure was higher, for at high pressure the value measured was much lower than the actual one.

On the other hand, the speed of pumping must not be too low because the diffusion of hydrogen through the surface makes the appearance of the bubble more difficult.

The speed of pumping is then limited only by the dead time of the measurement.

In a commercial apparatus it would be absolutely necessary to simplify the method of pressure reading. A push button operated by the observer would cause a hand to stop, thus giving the actual pressure.

The results of Messrs. Ransley and Mountford on hydrogen determination in high purity aluminum (99.8 pct) confirm my own results (99.99). In a similar case I have written that "any hydrogen determination with an acceptable accuracy is impossible."

Regarding the results of the determination carried out on a 99.2 pct aluminum, the departure of the correlation line from a 45° straight line can be due either to an increasing error of pressure reading when the hydrogen content rises, or to a variation in the nucleation conditions.

When the hydrogen content is higher than 0.30 cm³ per 100 g (Mr. Ransley's scale), the bubble pressure apparatus gives, for 8 measures out of 9 with exception of the "rogue point," lower values than the hot extraction process. But I have pointed out previously that an increase in the error of reading can easily occur with an increase of pressure when the speed of pumping is too rapid. The bubble pressure determinations reported in Fig 10 have been all carried out at about 700°C, therefore the pressure bubble formation increased with the hydrogen content and likewise a possible error of reading.

For hydrogen contents lower than 0.3 cm³ per 100 g nothing can be said, for in Fig 10 all these values are distributed at random; that would mean that for hydrogen contents lower than 0.30 cm³ per 100 g according to Ransley's scale and 0.090 cm³ per 100 g according to my scale, the bubble pressure apparatus could not be used. However Fig 2 and 3 of my first paper show that almost all the values are smaller than 0.090 and are not distributed at random but follow perfectly logical laws: hydrogen content increases during heating in a gas furnace and decreases during holding in a gas furnace (burners out) or in an electric furnace.

If the values of Fig 10 are not considered lower or higher than 0.3 cm³ per 100 g, but as a whole, the calculation of the correlation shows that they cannot give correct results. The application of the coefficient of correlation to the values given on Fig 2 of the paper would give a loss of only 0.04 cm³ per 100 g (Ransley's scale) or 0.012 (my own scale) by standing 2 hr in an electric furnace.

Such a small hydrogen decrease cannot be detected on the properties of an aluminum alloy (see for instance Fig 9 of the Ransley and Neufeld paper), while the effect of a 2 hr holding is well known by all aluminum foundrymen and can be very easily noted in the appearance of a vacuum sample.

Concerning the formation of a hydrogen bubble in an aluminum bath, it has been recalled in the paper that the hydrogen pressure in it was equal to

$$P_{H_2} = p_A + \frac{2n}{r}$$

and that the unobservance of the term $\frac{2n}{r}$ introduces a supplementary error which has been included in the term $\frac{df}{f}$ estimated by means of dispersion measures.

Therefore any direct comparison between bubble pressure and hot extraction measurements would be particularly welcome. Such a study would allow the analysis of the source and variation of

Table 8 . . . Value of Solubility Ratio

Metals	Mn	Fe	Ni	Cu	This Paper	Al Ransley and Neufeld
Solubility ratio	1.80	2.07	2.14	2.73	2.93	19
Log H_2 (H_2 being the solubility in solid state at melting point, expressed in *w* pct, P_{H_2} = 1 atm.)	−2.415	−2.922	−2.789	−3.753	−5.282	−5.49

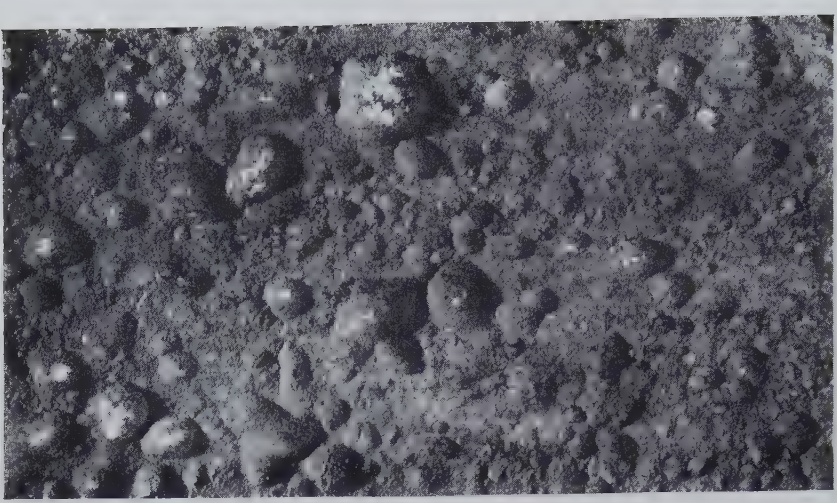

FIG 13—Aspect of surface of a wrought duralumin sample after 4 days heating at 560°C.
(Hot rolled down to 8 mm.)

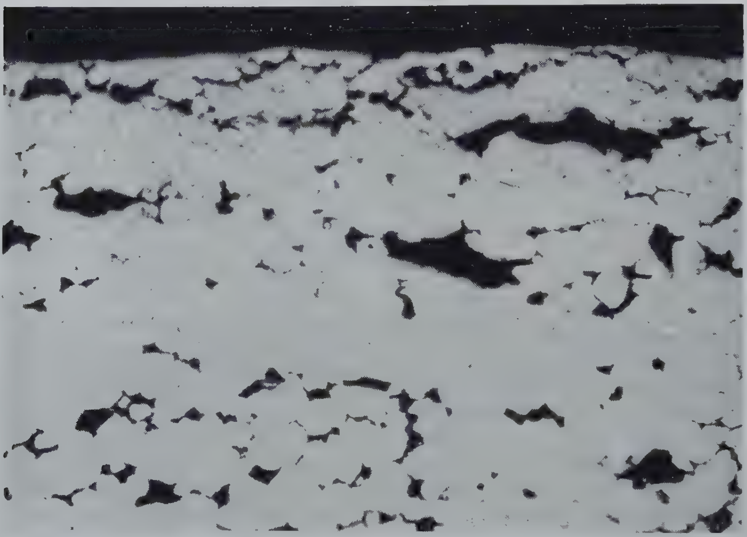

FIG 14—Formation of pores and blisters in wrought duralumin by heating at 560°C for 4 days.
(Hot rolled down to 8 mm.)

error represented by f, particularly the effect of the unobservance of $\frac{2n}{r}$ on its value.

It may be that this study would allow the estimation of the $\frac{2n}{r}$ value and through the introduction of a corrected pressure in Eq 4 more accurate results than those illustrated in Fig 5 might be obtained.

Reply to R. Eborall:

Mr. Eborall's discussion may at first seem to indicate that the determination by hot extraction of hydrogen contained in aluminum gives very accurate and indisputable results. However an examination of the papers cited by Mr. Eborall do not lead to such a conclusion. Sloman,[22] whose work on hydrogen determination in steel samples is now considered a reference in all laboratories of the Continent, tried to determine the gas content of aluminum samples with an apparatus similar to that used for steel. This author is quoted by Mr. Eborall as having given very accurate results. However, if Sloman's publication is one of the first to have cleared up the problem of gases in aluminum, the absolute values given are far from accurate in view of Ransley's work. For instance Table IV (Fig 40+) of Sloman's paper states that hydrogen in excess of that which fills voids of a porous casting is equal to 0.47–0.50–0.51. However, according to Ransley and Neufeld this value is about 0.12 cm³ per 100 g and, according to my own experiments expressed in Ransley's scale, about 0.15–0.20. The discrepancy is important. Regarding the results cited in Ref. 9, instead of discussing the difference between "adsorbed" and "surface" hydrogen—the first coming from hydrogen present in the atmosphere and adsorbed as such, while the second would come from the decomposition by heating of adsorbed water vapor—it remains that the surface correction was of the order of the measured value and Ransley and Neufeld[24] could write: "Eborall and Ransley estimated the solubility in commercial aluminum at 600°C to be approximately 0.10 cm³ per 100 g, but their method involved the subtraction of a large and rather uncertain correction from their measured value"; and Ransley and Neufeld now give a value of 0.026 as solubility at 600°C.

I have recalled these values not to point out these differences, but only to make clear that a hot extraction determination remains delicate even with the most accurate apparatus and is therefore always subject to error.

The method of estimating hydrogen content by measurement of the density of an aluminum sheet after heating between liquidus and solidus is perfectly logical and is of interest to all laboratories which do not possess a hydrogen determination apparatus. It proceeds from the old qualitative method of hydrogen estimation by observation of the appearance of a sheet heated at 560°C for one hour.

The method of Mr. Swain gives the total amount of dissolved hydrogen, but can be used only with wrought material (Fig 13 and 14). Any heating of a sheet milled in as cast material leads to the formation of channels through which dissolved hydrogen escapes (Fig 15–16).

On the other hand the measurement of the density of a casting gives only the amount of gas above the limit of solubility at melting point provided that no oversaturation occurs. In fact the hydrogen content of duralumin sheet must be far lower to make sheet weldable without any defect (Fig 17).

The penultimate section on hydrogen determination by hot extraction must not be separated from the context. It has to be applied to the usual hot extraction apparatus having an accuracy of only 0.2 cm³ per 100 g.

Regarding the amount of hydrogen which can be extracted from a sample I have shown (Table 4) that hydrogen content can be higher than the solubility limit at melting point when pores are present in casting. On the other hand with commercial aluminum and duralumin I have never observed less absorption of hydrogen even by one day heating in a vapor atmosphere (and subsequent turning of the sample). Sloman's Table VII[22] also could not detect any absorption of hydrogen after dipping of the samples in different solutions. Therefore if this way of gassing a sample is very common with iron, it is far from likely with aluminum.

The work of Klyachko has not been quoted to affirm that in any case aluminum is riddled by channels but only to make clear that in some cases, chiefly with castings on X ray examination, very high hydrogen content is sometimes observed. This can be explained by absorption of water vapor in microshrinkage which of course is not necessarily going throughout the metal.

The dispersion range of the liquid solubility data has already been discussed elsewhere. Therefore it will be enough to recall that the mean solubility datum given by Braun is not 0.08, but 0.24 cm^3 per 100 g at 700°C, 0.08 being only one of the figures. Moreover, the dispersion range of Röntgen and Braun, Röntgen and Möller, Bircumshaw and Winterhagen is rather small. However, it may be better to adopt the new values of Ransley and Neufeld, which confirm those of Baukloh and Oesterlen. If such a step is adopted all the data reported in this paper are homogeneous to those given in Ref. 24 and can be compared to them.

The difficulties due to nucleation have already been discussed in the reply to Messrs. Ransley and Mountford and therefore will not be repeated.

I should like to point out that I agree completely with the opinion of Mr. Eborall on the respective use of an accurate hot extraction apparatus and a bubble pressure apparatus. The new hot extraction apparatus giving absolute data would be used to provide calibration curves and check the results of a bubble pressure apparatus. But while the former can be used only in a few specialized laboratories, the latter can be employed not only in any laboratory, but also on any pouring platform.

At the time the experiments were begun, this distinction could not be made since the old hot extraction apparatus had an insufficient accuracy.

Reply to M. Bever:

I think that the internal pressure of all gases except hydrogen is very small in an aluminum bath. The gases according to Sieverts' law can be dissolved only as atoms or more likely as protons and the stability of oxide and nitride shows that all dissolved oxygen and nitrogen are practically bound to metal. Only methane can also be present in the bubble, but its pressure is about 100 times smaller than that of hydrogen (Fig 4). On the other hand, the dissociation pressure of Al_2O_3, and Al N or the pressure of CO due to the reaction of oxide or carbide is extremely small and can be neglected.

The experiments of Sloman as well as those of Eborall and Ransley confirmed this point: "Hydrogen in fact, appears to be the only gaseous element which is appreciably soluble in the metal in the temperature range normally considered."

It is quite certain that surface tension inhibits the formation of the bubbles, and I have admitted that the size range of the artificial nuclei was wide open and therefore that the effect of surface tension could be reflected in the dispersion of the determinations. However, as has been very clearly pointed out by Mr. Bever, the effect of surface tension on the scatter

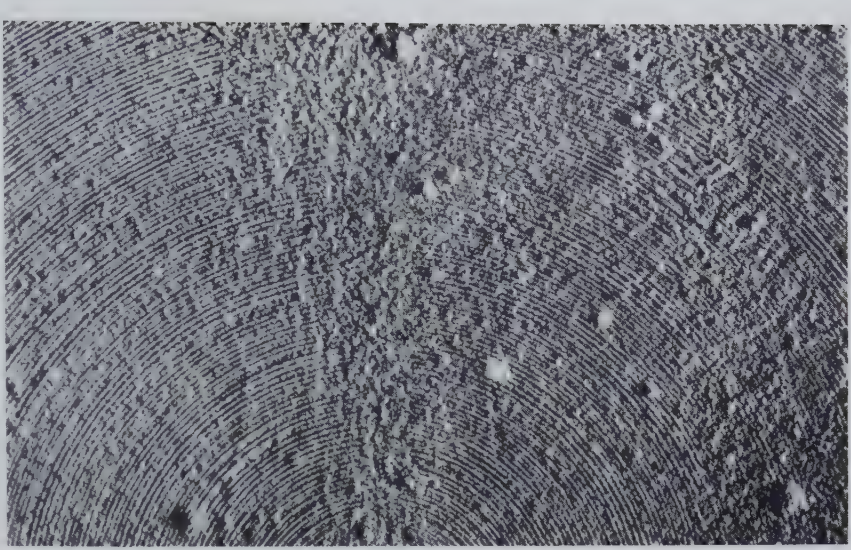

FIG 15—Aspect of surface of an as-cast duralumin sample after heating at 560°C for 4 days.
(Machined down to 3 mm thickness.)

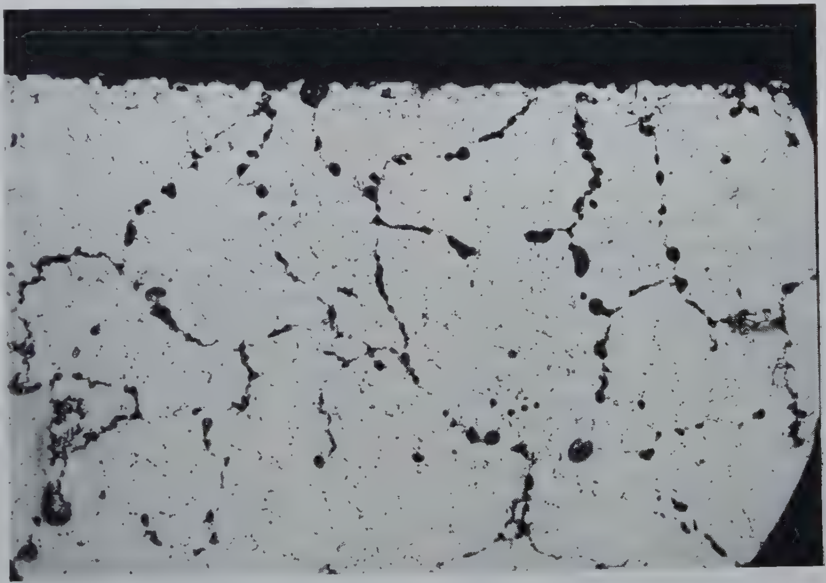

FIG 16—Formation of pores in cast duralumin after heating at 560°C for 4 days.
(Machined down to 3 mm thickness.)

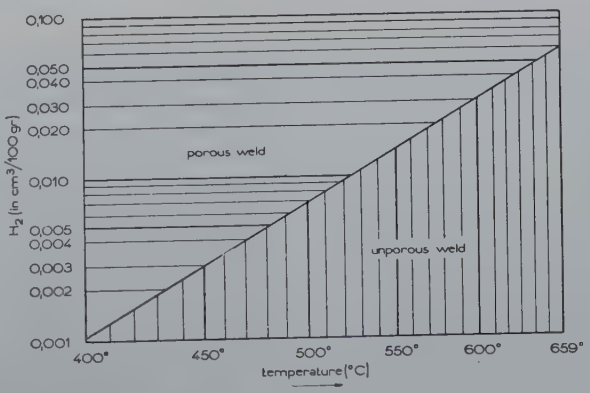

FIG 17—Relationship between the incipient melting temperature of an aluminum alloy and the maximum amount of dissolved hydrogen permissible for welding.

of the results remains small if all artificial nuclei have approximately the same size. Observations of oxides removed from an aluminum bath show that their surfaces present cavities which are not wet by the metal and which have a quite different size. However, a direct proof of the hypothesis which is the basis of Eq 3 can be made only through comparison of the results obtained by accurate hot extraction analysis and bubble pressure determination.

On the other hand I do not think that the experiments of Brower and Larsen can be opposed to the basic hypothesis as the experiments of Körber and Oelsen[35] show. According to these authors no formation of CO occurs when steel is melted under a silicate slag because the metal is enveloped in a hull of glassy silicate presenting no cavity acting as nuclei, while the boil starts as soon as the steel bath comes in contact with the crucible wall. An aluminum bath contains solid impurities presenting cavities and not glassy ones, therefore if the surface tension inhibits the formation of bubble, this inhibition remains small.

In fact, according to Ransley and Neufeld's determinations, the hydrogen content of an aluminum casting just free of pores varies between 0.12 and 0.18 cm^3 per 100 g (Fig 9 of their paper), while the determinations of this paper (Table 4) expressed in Ransley's scale give 0.15–0.20 cm^3 per 100 g. This agreement seems to offer proof that the hypothesis, which is the basis of Eq 3 can be accepted in first approximation, provided of course that the liquid solubility given in Ref. 24 is the correct one.

No calculation of the speed of hydrogen diffusion into the bubble has been carried out, but the speed of pumping being rather low the equilibrium in the bubble size does exist at any moment.

The very low diffusion speed of hydrogen through an oxide film has been clearly shown by Ransley and Neufeld. Fig 3 of their paper confirms the old hypothesis that the gassing and degassing rate of an aluminum bath is controlled by a surface phenomenon.

Reply to F. N. Rhines:

Mr. Rhines rightfully points out the importance of the adsorbed film on the result of a gas analysis, but I think that it would be very difficult to establish whether "surface hydrogen is coming from adsorbed hydrogen or from adsorbed "water vapor." On the other hand Schmid and von Schweintz as well as Chandron and Moreau have made an extensive study of the effect due to the ratio $\frac{\text{volume}}{\text{surface}}$ of the sample. As has been shown in the paper, the sample must be turned out and as soon as the ratio $\frac{\text{volume}}{\text{surface}}$ is lower than a certain value a correction factor has to be introduced.

Reply to E. A. Gulbransen:

Mr. Gulbransen points out that certain reactions can be the source of gases in hydrogen. In fact, as I have already explained in the reply to Mr. Bever, hydrogen is the only dissolved gas able to give bubble. On the other hand, the reaction of the water vapor of the atmosphere with the metal can occur only through the alumina film which, already impervious to hydrogen, shall be still more impervious to the diffusion of any big molecule.

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Plastic Deformation Waves in Aluminum

By A. W. McREYNOLDS

DISCUSSION

(R. S. Busk presiding)

E. OROWAN*—I observed the phenomenon of jerky yielding many years ago with zinc[25] and cadmium single crystals. A significant point was that the jerks occurred not only when the stress was raised but also (sometimes, after a pause of many minutes during which no trace of creep was observable) at constant stress. The phenomenon may be closely linked with the inertia of the testing machine and of the specimen, although the inertia alone cannot account for it. If, during the test, the resistance of the material to plastic deformation suddenly diminishes while the applied force remains constant, a sudden deformation follows until the yield stress has risen, by strain hardening, to the level of the applied stress (= the value of the previous "upper yield point."). When this is reached, the rate of deformation has attained a maximum value because, up to this moment, the applied force was higher than the plastic resistance of the specimen, and the difference was used for accelerating the moving parts of machine and specimen. The kinetic energy accumulated is now transformed into plastic work by further deformation; that is, the deformation overshoots the point at which the plastic resistance equals the applied static force. When the kinetic energy has been used up, therefore, we are left with a specimen the yield stress of which is higher than the applied stress, and no further deformation can occur (apart from a little creep) until either the applied stress has been raised to the new yield stress level, or the yield stress has fallen by thermal recovery to the level of the applied stress. While this occurs, a new upper yield point can develop, for example, by precipitation.[26]

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* Cavendish Laboratory, Cambridge, England.

[25] E. Orowan: *Ztsch. f. Phys.* (1934) **89,** 634.

[26] A. H. Cottrell and D. F. Gibbons: *Nature* (1948) **162,** 488.

There is no intrinsic contradiction in the assumption that thermal softening (by the removal of internal stresses) and precipitation hardening can occur simultaneously. The hardening effect of precipitations may be overcome by a small deformation which tears away the encircling dislocations from the precipitates,[27] and then the softness of the material, acquired by thermal recovery, may reveal itself. In this way, the inertia of the testing machine and of the specimen may contribute essentially to the development of upper yield points during the test, not only to the size of the jerk when an upper yield point is overcome.

Jerky extension need not be connected with the propagation of a plastic wave along the specimen. I investigated this question in 1940 for Cd crystals; the work was interrupted by the war and has not been published. I stuck nearly close-packed rows of minute shiny spheres of pure tin (about 1/1000 in. diam each) to single crystal wires parallel to the wire axis; the spheres were produced by dropping filings of tin into a bath of molten stearine, the top part of which was above, and the bottom part below, the melting point of tin. The single crystal with the row of tin beads was illuminated with a distant pointolite lamp, and photographed, at about × 20 to 50, with a rotating drum camera; the reflections from the beads traced extremely sharp lines on the recording paper, and the record showed directly which parts of the specimen had undergone plastic deformation: every pair of beads acted as an extensometer over a gauge length of a few thousandths of an inch. The records showed that the extension jerks were localized in a very short part of the specimen where, as a rule, many consecutive jerks occurred.

The presence of an upper yield point, if this is not re-formed during the experiment, need not cause any further jerkiness of the deformation. We are carrying out experiments on the propagation of Lüders bands in mild steel wires in the Cavendish Laboratory (with Mr. W. Sylwestrowicz); in these experiments, only one Lüders band arises (usually in one of the grips, unless the ends of the wire are provided with electrodeposited heads), and this spreads over the wire in a perfectly continuous way, as slowly as is required, under a practically constant load. An essential condition of this, of course, is that the testing machine and the dynamometer must be very rigid.

E. H. DIX*—We think there is a rather clear-cut correlation between the irregular yield point elongation and the tendency to form Lüders lines. In the case of aluminum alloys containing several per cent magnesium, we get quite jagged yield point elongations and also the formation of strain lines in certain articles in which the metal is stretched in some locations during forming. In the case of annealed material, a small amount of cold work by rolling, or even by running the sheet through a series of offset rolls, that is, a roller leveler, the tendency to form Lüders lines is reduced.

Another observation is in connection with the duralumin-type alloys. Immediately after quenching, while they are in the rather unstable condition, there is a marked tendency for the Lüders lines to form, and if you watch a specimen being tested in tension you see the lines running up and down the gauge length of the specimen. It is a very interesting phenomenon to watch. After a few hours of aging that tendency disappears, and certainly after a day of aging the Lüders lines are not seen, and the yield point portion of the curve is smooth and not jagged.

R. S. BUSK†—It seems to me that one of the important points in this paper is that the phenomenon of yielding and the increase in stress necessary for subsequent yielding are so uniform. Any explanation must take into account the fact that the steps increase in a linear fashion. I wonder if simply tensile machine inertia forces would result in such a uniform step pattern.

A. W. McREYNOLDS (author's reply)—As Dr. Orowan points out, there is considerable diversity in the manner in which irregularities in the stress-strain curve occur in different materials, as illustrated by his interesting observations on cadmium, zinc, and mild steel. It seems nevertheless profitable to view the spread of deformation through the metal as propagation of a plastic wave, even though the wave extends only through a limited region, as in Orowan's observations on cadmium and the author's observations on aluminum-copper, or spreads very slowly, as in mild steel. Whatever the mechanisms of thermal softening, precipitation hardening, and others, involved it seems clear from the continuous spreading of deformation that plastic yielding of the hardened lattice does not occur uniformly over an extended region but is initiated in the small region of inhomogeneous stress at the boundary between deformed and undeformed material. Thus a complete explanation of the phenomenon must take account of stress concentrations ahead of the plastic wave in addition to such overall properties of the material as yield stress.

As both Mr. Busk and Dr. Orowan commented, inertial effects in the tensile machine and even in the specimen itself may strongly influence the discontinuous yielding phenomena. It seems likely that most of the results to be found in the literature are complicated by this factor. The soft tensile machine used in the present experiments was specifically designed, however, such that inertial effects are eliminated insofar as possible by applying tension through a coil spring to eliminate both mass and variations of load on yielding. It is believed that, as a result of this and other special precautions, the instrumental inertia effect had no significant effect on the observed irregularities in plastic yield.

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[27] E. Orowan: Discussion at Symposium on Internal Stresses. London 1947 (Inst. of Met. Monogr. Series No. 5, p. 451).

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† Dow Chemical Co., Midland, Mich.

Homogeneous Yielding of Carburized and Nitrided Single Iron Crystals

By A. N. HOLDEN and J. H. HOLLOMAN

DISCUSSION

(R. S. Busk presiding)

A. H. COTTRELL* and A. T. CHURCHMAN*—We have been making some experiments recently very similar to those reported by Messrs. Holden and Holloman. Wires of Armco iron, 0.077 in. diam, were decarburized in wet hydrogen until the yield point was removed; they were then extended 3¼ pct and annealed at 880°C for 120 hr in dry hydrogen. This process produced large crystals which extended through the cross-section and were about ¾ in. in length. Since the length of each crystal was thus about ten times its diameter, wires prepared in this way behaved as single crystals in tensile tests and no attempt was made to grow longer crystals. The wires were carburized by heating at 720°C for 1 hr in propane and then annealed at 680°C for 65 hr in argon. This treatment was sufficient to cause the return of a sharp yield point in polycrystalline specimens.

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Before testing the crystals preliminary experiments were made to develop a method of mounting them in the testing machine; the criterion taken for a satisfactory technique was that it should permit the observation of a very sharp yield point, considerably higher than the lower yield point, on a carburized polycrystalline test-piece of the same form as the single crystal specimens. Eventually a procedure was adopted which used a 5 in. wire, the ends of which were tinned for a distance of 2 in., as a test piece. Each end was inserted to a depth of 1½ in., and soldered, in an axial hole in a ⅜ in. diam steel rod, 3 in. in length, the other end of which was attached to a shackle of the testing machine by a 5 in. piece of fine, flexible steel cable. A standard lever machine was used and the extension was measured by a screw attached to its cross-head, no extensometer or other attachment being mounted on the specimen. With this arrangement very sharp upper yield points at stresses of about 30,000 psi could be obtained consistently on polycrystalline specimens, the corresponding lower yield points occurring at about 25,000 psi.

Several single crystal specimens were tested by this method and Fig 15 shows typical results obtained. No yield point was observed on hydrogen treated specimens and extensive plastic flow began at a stress of about 4500 psi, in agreement with Holden and Holloman's results; furthermore, no yield point was developed by unloading overstrained specimens and aging them at 100°C for a few hours (*curves* 3, 5 and 7).

The carburized crystals, on the other hand, showed yield points. Fig 1 shows an example of this, together with the effect of overstrain in removing the yield point (*curves* 2, 4, 6, 8 and 10 were taken immediately after unloading) and the return of the yield point at a higher stress level on strain aging (*curves* 3, 5, 7 and 9 were taken after aging the unloaded specimen at 100°C for a few hours). The lower yield point is first observed at a stress of about 7500 psi, but a clearly marked upper yield point does not appear until the yield point has been raised, by strain aging, to about 15,000 psi.

While these experiments have shown the existence of inhomogeneous yielding in carburized iron crystals, they raise several questions, quite apart from the fact that they give a different result from that of Holden and Holloman's experiments. For example, why is the yield point so small at first, compared with that of a polycrystalline specimen, and why does the upper yield point only appear after strain aging? To help answer these questions, we are at present examining the effects on the yield point of such factors as, for example, the depth of penetration of the carburized region or the condition of the surface of the specimen.

L. D. JAFFE*—It is very gratifying to be able to deduce from these new experiments that the old idea that the yield point in steels is associated with the grain boundaries, is apparently correct. It is not so gratifying, however, if we try to draw some general conclusions about the nature of the yield point phenomenon, when we remember that in brasses the yield point does appear in single crystals, and perhaps more so in single crystals than in polycrystalline material. That is unfortunate, because we would like to have similar explanations for similar phenomena. Would Mr. Holden give us any ideas he may have as to why this difference exists between behavior in brass and steel?

A. N. HOLDEN (authors' reply)—The yield point has been observed of course in single crystals of materials other than iron. For many years the yield point has been known to occur in cadmium and zinc crystals. I believe in these cases it was observed only as a consequence of strain aging. Cottrell and Gibbons[11] found that nitrogen was a necessary impurity in the case of cadmium.

Unfortunately I have no ready explanation for the phenomenon Mr. Jaffe described concerning yield points in brass crystals.

E. OROWAN†—The authors have performed an experiment of great importance to the theory of the yield phenomenon in steel. As far as I know, Dr. Cottrell and his collaborators in Birmingham, England, have been working on the same experimental problem for the last year or two, and it will be interesting to compare their results with the present ones.

With the experiments of Holden and Hollomon, the situation in the theory of the yield phenomenon has become particularly interesting. With steel, the phenomenon occurs only in a sufficiently fine-grained polycrystalline material; with zinc and cadmium, only in single crystals.[12] It seems fairly clear why it is not observed in polycrystalline zinc or cadmium. Having only one set of easy slip planes, the grains of these metals cannot conform easily with the deformations of the neighboring grains, so that the yield stress of the polycrystalline material is many times higher than that of a single crystal of average orientation. Since the upper yield point of Zn or Cd crystals is never more than 30 to 50 pct higher than the lower yield point, it cannot be observed in a polycrystalline metal which does not yield in any case before the average yield stress of the individual grains is exceeded by several hundred per cent.

It seems that there are (or, there had been before the experiments of the authors) three survivors among the numerous theories of the yield phenomenon. The oldest among these is the hypothesis that there is a thin film of cementite at the grain boundaries which breaks when the upper yield point is reached (Ludwik, Nádai, and Kuroda). Edwards, Phillips and Liu[13] abandoned this view when they observed that the yield phenomenon occurred in several nonferrous alloys only after a slight preliminary straining followed by annealing. In place of the cementite boundary layer hypothesis, Edwards, Phillips and Liu introduced the assumption that the yield phenomenon was due to a precipitation along the active slip planes.

In Cottrell's view,[3] invisibly thin films of cementite could not account for the high values of the upper yield point observed in steel. He attributes the yield phenomenon to the accumulation of carbon atoms on the tensile side of dislocations where the atomic lattice is expanded; this process would reduce the energy of the dislocation, and an additional stress would be necessary to tear it away from its carbon atoms. If this is the cause of the yield phenomenon, single crystals ought to show it equally well; in fact, for the reason I have mentioned in connection with zinc and cadmium, they ought to show it rather better than polycrystalline material.

At first sight, it would seem that there is very little difference between the slip plane precipitation hypothesis of Edwards, Phillips and Liu, and the hypothesis of Cottrell; in reality, the difference is very significant. Of course, the particles precipitated in operative slip planes must have been nucleated at dislocations, for the presence of these is the only thing that makes an operative slip plane differ from plastically undistorted parts of the crystal. With this, however, the common ground of the two hypotheses ends. Cottrell assumes that a perfect crystal would be very hard; only the presence of dislocations makes it relatively soft, and it must become harder if the dislocations are made less effective by being clogged with carbon atoms. On the other hand, the slip plane precipitation hypothesis assumes that the "softest" individual slip planes in the

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[11] *Nature* (1948) 162, 488.

[12] E. Orowan: *Ztsch. f. Phys.* (1934) 89, 634; C. L. Smith: *Nature* (1947) 160, 466.

[13] C. A. Edwards, D. L. Phillips, and Y. H. Liu: *Jnl.* Iron and Steel Inst. (1934) 147, 145.

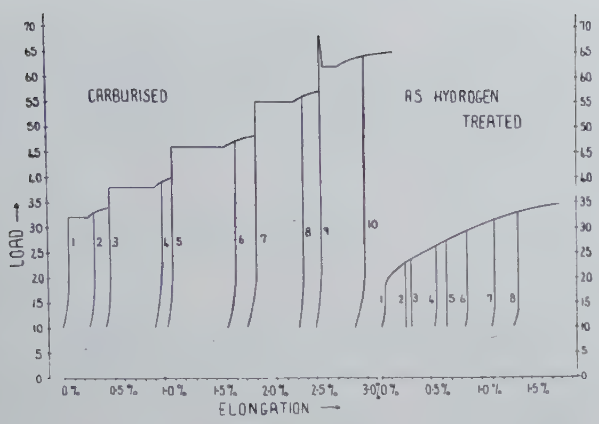

FIG 15—Load elongation curves showing the yielding behavior of carburized and decarburized iron crystals.

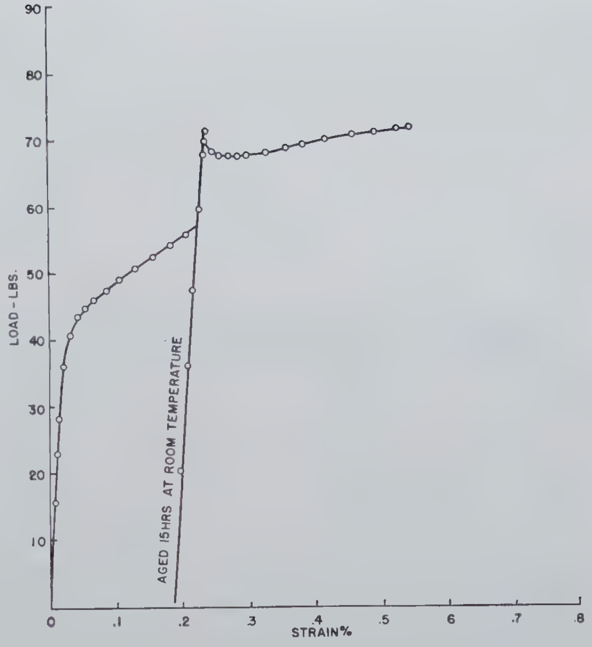

FIG 16—Strain aging of a carburized iron crystal.

material, on which slip starts first, are subsequently immobilized by local precipitation hardening. The hypothesis of the clogged dislocations cannot be applied whenever prestraining is necessary for the development of the yield point; in an annealed material, there should be either no dislocations present, or only a few clogged ones, and in either case there should be an upper yield point. On the other hand, it is not easy to see how the slip plane precipitation hypothesis could explain the yield phenomenon in annealed (unstrained) materials.

Both the hypothesis of the clogged dislocations and that of slip plane precipitation might seem to face difficulties in explaining the grain size effect. It appears, however, that an explanation on this basis is not quite out of the question. In a polycrystalline metal, the interference of the neighboring grains may reduce the planes of easy slip to a small number which can be immobilized by precipitation; in a single crystal there may be numerous almost equally favorable slip planes, and even if many of these are immobilized, there are still many left on which slip may start at a not much higher stress. In this way, the slip plane precipitation hypothesis might lead to a certain grain size effect. This possibility does not exist for the hypothesis of the clogged dislocations; a grain size effect could arise here only if the important dislocations are at the grain boundaries. Since the yield phenomenon in steel needs no prestrain to arise, these dislocations must be the ones determined by the geometry of the lattice misfit between the neighboring grains, and the hypothesis is then reduced to what amounts to a re-interpretation of the boundary cementite hypothesis.

The conclusion seems to be that the cause of the yield phenomenon in steel is probably different from that in zinc, cadmium, or silver. In the latter cases, the slip plane precipitation hypothesis is very plausible; in the case of steel, the effect is probably due mainly to the resistance of the grain boundaries to slip being increased by some precipitation, in the manner expressed crudely by the cementite film hypothesis.

A. N. HOLDEN—I wish to thank Dr. Orowan for indicating the importance of those experiments to the theory of the mechanical behavior of metals. His remarks indicate the need for a thorough experimental attack on the problem of strain aging of single crystals.

A. N. HOLDEN and J. H. HOLLOMON—The experiments of Cottrell and Churchman are very interesting, since the explanation of the yield point by Cottrell[3] was somewhat embarrassed by the failure of our carburized or nitrided crystals to yield discontinuously. The unfortunate circumstance of a difference in the results of Cottrell and Churchman and the authors now exists. Furthermore, in an as yet unpublished paper,* Schwartzbart and Low have observed a horizontal portion of about 0.2 pct in extent in the stress-strain curve of single crystals of iron upon initial yielding.

This discrepancy might be explained in several ways:

1. An unlikely source of the discrepancy is the aluminum content of our crystals (an element absent or low in Armco iron). Aluminum might be expected to affect the results of nitriding, but should have no effect upon the carburized specimens. Still another material, a silicon-killed steel, was used in making the crystals tested by Schwartzbart and Low.

2. Perhaps the fine wires employed by Cottrell and Churchman were strained before testing (deformation of the wires would be difficult to prevent in handling), and even the initial yielding of their crystals arose from strain-aging.

3. The difference in the heat treatments accorded the crystals in the several experiments might lead to the different results. It is quite possible that the rate of cooling from the homogenizing temperature could affect the results. For instance, rapid cooling might introduce quenching strains allowing the crystal to strain-age prior to testing.

4. It is also a possibility that the authors (Holden and Hollomon) did not align their crystals as accurately as necessary for specimens of the shape used in the experiments. Alignment of these specimens is a serious and difficult problem, particularly if the initial yield point elongation is very small. It must be admitted, however, that with a yield point elongation of 0.2 pct such as Cottrell and Churchman observe, the misalignment would have to cause differences of this amount in strain on the two sides of a crystal to obscure the effect. The authors feel that they achieved sufficient alignment to reveal a 0.2 pct yield point elongation, but they are continuing to direct their efforts toward the development of better means of axial loading.

5. No doubt Cottrell and Churchman have considered the consequences of carburizing so close to the critical temperature. After 1 hr at 720°C in a propane atmosphere their crystals would undoubtedly be saturated with carbon. During this treatment any accidental temperature fluctuation to approximately 725°C would result in the formation of polycrystals.

Cottrell and Churchman have shown that carburized iron crystals will undoubtedly strain-age. This information will be a valuable aid in understanding the yield point phenomenon.

Since this paper was written, many experiments have been conducted by the authors on the strain-aging of iron crystals made of carburized aluminum-killed steel. It is of interest to compare the results of one such experiment with those of Cottrell and Churchman. Fig 16 shows the yielding of a carburized crystal. Initially there was no sign of a yield point or discontinuity. After straining 0.18 pct, unloading, aging 15 hr at room temperature, and re-straining, a definite upper yield point was observed, together with some 0.1 pct yield point elongation.

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* Unpublished at the time of AIME San Francisco Meeting, Feb. 1949.

Temper Brittleness of Plain Carbon Steels

By L. D. JAFFE and D. C. BUFFUM

DISCUSSION

(*R. E. Leiter presiding*)

M. G. CORSON*—The low temperature brittleness of carbon steels rapidly progresses with the increase in the carbon content. The presence of nickel greatly counteracts that brittleness. For this reason a comparison of a high nickel, low chromium steel of 0.39 pct carbon content to a carbon steel of 0.47 pct C is not warranted.

Having committed this error the authors ought to present at least a table of characteristics in the static test to show that the two steels were essentially identical.

Rockwell C values of 18–19 are rather meaningless. Brinell or Rockwell B figures should have been given.

The authors succeeded only in proving that a 0.47 pct C steel of unknown characteristics tempered at 675°C for a very short period after being water-quenched (this introduces irreparable amounts of brittleness anyway) was *sharply* brittle at about −60°C; while an alloy steel containing less carbon and quite a lot of nickel was *not so sharply* brittle in the same range.

It might have been much more to the point if the authors had examined the relative brittleness of steels of the same carbon content, one without and another with a substantial amount of chromium, but just the needed amount of Mn (0.8 pct is much too much for a plain carbon steel). Then both steels should be oil quenched and tempered at a moderate temperature (about 400°C) followed by testing at room temperature, because it is fundamentally the brittleness of troostitic steels under normal conditions that causes misgivings.

Furthermore: Half size impact test-bars should be used only in such cases where the finished piece is very small in its cross-dimensions. It is almost a foregone conclusion that full-size test bars would have shown a rather different behavior.

L. D. JAFFE and D. C. BUFFUM (authors' reply)—It is always interesting to get a discussion from Mr. Corson. We will cover a few of the points he has raised. We were not aware that the presence of nickel counteracts temper brittleness in any sense. It has always been felt that there are considerable data indicating that nickel increases temper brittleness. With respect to manganese, the manganese contents were the same in the two steels, and they were within the specified limits for those particular S.A.E. steels.

Mr. Corson would like us to have used troostitic steels and test at room temperature. We explained in the paper why martensitic steels were desirable and why it is necessary to test over a range of temperatures. We also explained that half-size test bars had to be used in order to get martensite. A comparison was made of the behavior of those small size bars with that of full-sized bars, and the results are about to be published.[14]

J. K. Y. HUM*—We can substantiate the results Mr. Jaffe has given on using half-size sharp bars, except our steel was an SAE 1055 steel. We achieved comparable results with his with 1040, however there is a little question about this reduced toughness of plain carbon steels. At U. C. we investigated temper brittleness by the effect of alloy elements on high purity steels. We found that with plain carbon steels of high purity (without all the usual impurities that occur in the plain carbon steels), we got a decidedly greater toughness than normally occurs with commercial plain carbon steels. Regarding the effect of alloying elements changing the transition temperature, this is quite true with one exception, which is manganese. We found small amounts have a tendency to shift to a higher shifting temperature. There might be a qualifying statement to the alloying element in regard to manganese. That has a tendency to put a question mark on what happens to the embrittled curve.

In regard to other elements, we have done a reasonable amount of work with carbon chrome steels. We found that there is a certain amount of chrome necessary before the steel shows temper brittleness. Normally with steels up to and including 3 pct chrome temper brittleness is not evident. With over 3 pct it becomes quite temper brittle.

L. D. JAFFE and D. C. BUFFUM—We interpreted Mr. Hum's last remark to mean that in the lower chromium steels with no other alloys present there was no appreciable difference in transition temperature between the specimens slow cooled and those quenched from the draw. This, of course, may not necessarily prove that the steels are not susceptible to temper brittleness. They may have been embrittled in both conditions.

J. K. Y. HUM—That was a full-sized bar. It was not until we changed over to the half-size that we discovered the embrittlement you observed.

E. OROWAN*—In the Cavendish Laboratory, Dr. J. Nutting has studied temper brittleness by making aluminum pressings from the surfaces of fracture and examining the aluminum oxide film replicas obtained from these by the electron microscope. In all cases of true temper brittleness, the fracture was substantially intergranular, while the ordinary "notch-brittle" fracture of steel is substantially intracrystalline (cleavage fracture). If Dr. Nutting's results can be generalized, temper-brittleness is due to a lowering of intergranular cohesion, probably by some precipitation. A polycrystalline metal has, in principle, two brittle strengths: one for intergranular, and another for intracrystalline fracture. Typical temper brittleness appears when the intergranular strength drops below the intracrystalline one. A certain treatment of the material may produce brittle fracture by reducing either the intergranular strength, or the cleavage strength of the grains. Only in the first case are we entitled to speak of temper brittleness in the usual sense of the word. I should like to ask Mr. Jaffe, therefore, whether he and Mr. Buffum have studied the nature of the fractures microscopically or electron-microscopically in order to recognize whether the fracture was mainly intergranular or mainly intracrystalline.

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* New York City.

[14] D. C. Buffum: Investigation of Square Subsized Charpy Specimens. Accepted for publication, A.S.T.M. Bulletin.

* Univ. of California, Berkeley, Calif.

* Cavendish Laboratory, Cambridge, England.

L. D. JAFFE and D. C. BUFFUM—We are most interested to hear of the Cambridge electron-microscope results, which are in accord with findings of the optical-microscope.[15,16] Miss M. R. Norton at our laboratory has also been using the optical microscope in studying the path of fracture in temper brittle steels broken at temperatures below the transition range. She has not observed as clear-cut a distinction as Dr. Orowan indicates. The embrittled specimens had primarily an intergranular fracture but there was a considerable percentage of transgranular fracture. This was often somewhat rough, suggesting that a certain amount of local deformation occurred even though the fractures appeared brittle macroscopically and absorbed little energy. In the nonembrittled specimens very little of the fracture was along grain boundaries. These transcrystalline breaks appeared to be partly by cleavage and partly with local deformation.

In response to Dr. Orowan's last question, preliminary examination of the plain carbon steel fractures has been made by Miss Norton. The fracture path appeared to be predominantly intergranular on specimens which had been embrittled either by slow cooling or isothermally. Fracture in the unembrittled specimen was chiefly transgranular. Observations of the nature of the fractures thus support the hypothesis outlined in the paper.

J. MALTZ*—The two hypotheses described by the authors are not the only possibilities. It may simply be that the plain carbon steels are inherently less tough than alloy steels—that is, have higher transition temperatures in the absence of any embrittlement reaction.

This third hypothesis can lead to predictions (3) and (4) and reject predictions (1) and (2) just as well as the more complex one advanced by the authors. Nor is it unreasonable. Small alloy additions increase the inherent strength of ferrite, so why not the inherent toughness?

If we compare Hollomon's data[6] for a plain carbon steel (0.39 pct C, 0.85 pct Mn), water quenched, with the data of Archer, Briggs, and Loeb[17] for a chromium-molybdenum steel (0.39 pct C, 0.65 pct Mn, 0.57 pct Cr, 0.15 pct Mo) sensitized for 10 hr at 1025°F and furnace cooled, we find that the carbon steel has the higher transformation temperature. According to the authors' hypothesis, then, the plain carbon steel has more nearly completed the embrittlement reaction than has the chromium-molybdenum steel—though the time at reaction temperature was smaller by a factor of many thousand. It would be surprising if so small an alloy addition had so great a retarding effect on any reaction.

The slight differences which the authors report in an SAE 1045 steel, before and after embrittling treatments, may be caused by the relatively high manganese content, 0.81 pct. Previously published work[17] indicates that carbon steels do not show such differences if the manganese content is below 0.60 pct.

L. D. JAFFE and D. C. BUFFUM—It is true that small alloy additions increase the strength of ferrite. The reason is well understood: foreign atoms in solid solution within a lattice make slip more difficult. There are no theoretical basis and no experimental data to support the belief that alloys would make ferrite tougher. On the contrary, their strengthening effect would itself be expected to make the material less tough.

The data of Hollomon[6] cited by Mr. Maltz refer to a plain carbon steel air-cooled from the austenitizing temperature, whose microstructure would consist of tempered pearlite and primary ferrite. The data of Archer, Briggs, and Loeb[17] concern a fully-hardened alloy steel, whose microstructure would consist of tempered martensite. It is well known that pearlite-ferrite mixtures have much higher transition temperatures than tempered martensites[18] (other things being equal), so Mr. Maltz's comparison throws no light upon the temper brittleness of the steels. It may be noted, however, that moderate additions of molybdenum do retard one reaction—the transformation of austenite to pearlite and proeutectoid ferrite—by at least a factor of a thousand.[19]

We agree with Mr. Maltz that the slight differences in the SAE 1045 before and after embrittling treatments may be caused by the relatively high manganese contents.

Before closing we should like to mention a discussion that was submitted to us through private correspondence by the late Mr. Ernest Teichert of Pennsylvania State College. Mr. Teichert asked about the effects of longer embrittlement treatment. If our theory is correct, he pointed out, the carbon steel should show no additional embrittlement. As a result of this suggestion we have given the plain carbon steel a treatment of 500 hr at 455°C. The transition temperature was the same as for the 50 hr treatment.

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[15] D. McLean and L. Northcott: Micro-Examination and Electrode Potential Measurements of Temper Brittle Steels. *Jnl.* Iron and Steel Inst. (1948) 158, 169–177.

[16] P. V. Riffin: Unpublished work, Watertown Arsenal.

* U. S. Naval Gun Factory.

[17] R. S. Archer, J. Z. Briggs, and C. M. Loeb, Jr.: Molybdenum. Climax Molybdenum Co., 1948, p. 5.

[18] J. H. Hollomon, L. D. Jaffe, D. E. McCarthy, and M. R. Norton: The Effects of Microstructure on the Mechanical Properties of Steel. *Trans.* ASM (1947) 38, 807–847.

[19] J. R. Blanchard, R. M. Parke, and A. J. Herzig: The Effect of Molybdenum on the Isothermal, Subcritical Transformation of Austenite in Low and Medium Carbon Steels. *Trans.* ASM (1941) 29, 317–338.

Some Factors Affecting the Rate of Grain Growth in Metals

By J. E. BURKE

DISCUSSION

(S. E. Maddigan presiding)

S. E. MADDIGAN*—Dr. Orowan made the remark that in the field of cold-working of metals there was still room for a great deal of work, and he estimated it would be at least two decades before the subject became a finished article. I think in the field of recrystallization and grain growth, while it may not take two decades, there are still a great many questions to be answered, and it is extremely fortunate that since the war there have been several groups in this country able to devote attention to a continuous study of such fundamental problems. The present paper for instance

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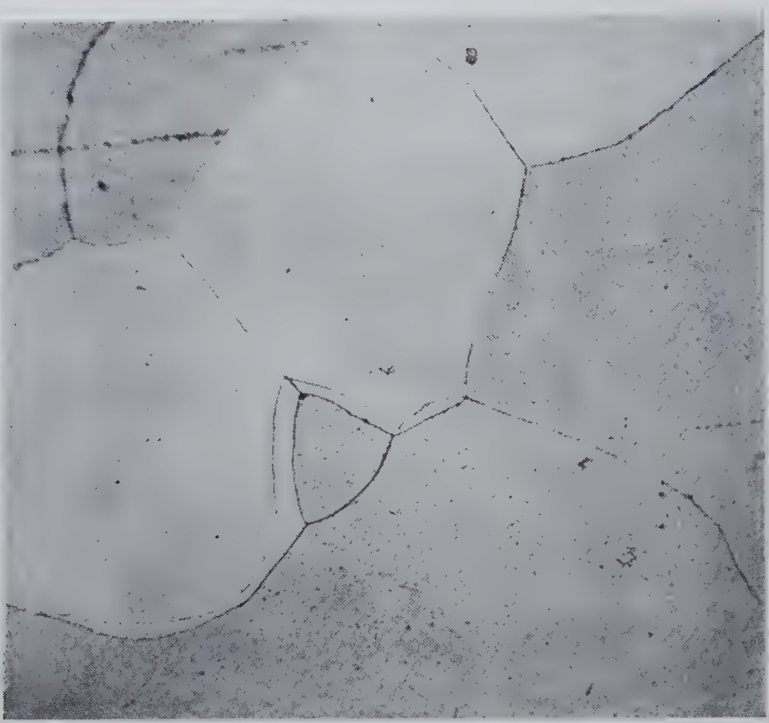

FIG 21—A time lapse micrograph illustrating a small grain in the plane of polish absorbing its larger neighbors.

The boundary migration of the small center grain is in a direction opposite that of the center of curvature of the migrating boundary.

is one of a series devoted to answering some of the questions connected with grain growth.

G. W. WENSCH*—It is readily apparent to those of us interested in the coalescence behavior of metals, that this paper is an excellent contribution to the literature. Furthermore, due to the fine control measures used in the experimental technique, the previous divergences existing between the data of Walker[4] and Beck[3] can be explained.

In observing many micrographs illustrating grain growth in metals it appeared that Harker and Parker's[9] hypothesis was correct in that boundary migration moved in a direction toward the center of curvature of the migrating boundary. However in Carpenter and Elam's[16] study on grain growth in antimony-tin alloys it was found that the migrating boundary can move in a direction opposite to that of its center of curvature as shown by Fig 21.

Since the existing theories do not satisfactorily explain the anomalous behavior cited above, could the author be induced to comment on this apparent oddity? Can the author now justify the use of Eq 3 as a basis for his derivation of Eq 7?

C. G. DUNN†—I would like to congratulate the author for his beautiful piece of work on the source of energy, the driving force for grain growth. Regarding the source of energy, I might comment on the question just raised by Mr. Wensch in connection with the work of Carpenter and Elam. Their material was in a strained state, I believe. The picture is entirely different if the metal is strained for a boundary may then move away from its center of curvature. The process may still be of the nature of grain growth. Dr. Burke did some work himself showing that grain growth can occur in material slightly strained, and in cases of that type, the strain energy in the crystals adds to the driving force.

The type of grain growth considered in the present work was clearly stated in the text. Some comments on this subject, however, may be worth making. There are two types of grain growth. First there is normal grain growth, or continuous grain growth according to Professor Beck. The thickness of the sample is a limiting factor with normal grain growth. The second type is usually referred to as exaggerated grain growth, but Professor Beck calls this discontinuous grain growth. As Dr. Burke points out in the paper, the effect of sample thickness is different for exaggerated grain growth; the final grain size is entirely independent of the thickness of the material.

I would like to discuss the picture that Dr. Parker presented on the 120° angles because it is based implicitly on the assumption that the driving force or surface tension is a constant and is independent of relative orientation. Surface tension, I believe, clearly depends on difference in orientation of adjacent grains. Data have been obtained showing that angles can depart quite far from the 120° value.[17] Such variations complicate the geometrical picture a little, but I would agree with the author and Dr. Parker that the geometry is a very important factor in grain growth processes. I would question the 120° angle, however, as being particularly important. I think the 120° angle may be a sort of average value which may be seen more often than any other angle, but it is somewhat of a coincidence when only 120° angles are obtained.

E. A. GULBRANSEN*—I am concerned about the interpretation of the activation energy in Eq 2 and 8. It would be an advantage to relate the energy of activation found for the rate of grain growth to a diffusion process. If this could be done H would have a physical meaning and the value could be compared to values of H obtained from other experiments. The value obtained for H, namely, 60,000 cal per mol appears very large for a diffusion mechanism.

P. A. BECK†—The suggestion that the various structural changes occurring in cold worked metals upon annealing are the result of the surface energy associated with the internal surfaces appears to have been first clearly formulated by G. Tammann in 1912.[18] As originally proposed, this theory was supposed to apply to *both* processes which usually take place under such circumstances, namely recrystallization and grain growth. Bengough and Hudson[19] noted as early as 1910 that recrystallization may lead to grain refinement. The subsequent studies of Chappell[20] on iron and of Mathewson and Phillips[21] on brass definitely proved that in the first stages of recrystallization after severe deformation, numerous small new grains are formed within each one of the deformed original grains. Mathewson and Phillips clearly realized that the "disintegration" of each deformed grain into numerous smaller ones during recrystallization is tantamount to an *increase* in the grain boundary surface energy, and that this energy increase must be supplied by that part of the strain energy absorbed by the metal during deformation. A detailed and lucid discussion of the energetics of recrystallization and of grain growth was given by H. Althertum in 1922,[22] who carefully differentiated between these two processes, and correctly identified the driving force of grain growth (in contrast to that of recrystallization) as the surface energy connected with the grain boundaries. His views had been accepted by most research workers for a number of years, without much further investigation of the details of the grain growth process.

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[16] H. C. H. Carpenter and C. F. Elam: Crystal Growth and Recrystallization in Metals. *Jnl. Inst. of Metals*, (1920) 24, 83.

[17] C. G. Dunn and F. Lionetti: The Effect of Orientation Difference on Grain Boundary Energies. *Jnl. of Metals*, Feb. 1949, 125. *Trans.* AIME (1949) 185.

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It was Harker and Parker's accomplishment[22a] to give a more detailed picture of the mechanism of grain growth in terms of movements of individual grain boundary surfaces and vertices, as described in the present paper by Burke. Recently C. S. Smith[22b] elaborated upon Harker and Parker's proposal and contributed important refinements to the theory. Burke's experiment with partially melted brass may be considered as the first direct proof of Harker and Parker's ideas. The old and familiar concept that small crystals, surrounded by the mother liquor, are unstable in the presence of larger crystals of the same species, will have to be discarded if the basic features of the Harker-Parker theory are correct. If both the small and the large crystals are idiomorphic, according to this theory the atoms at their corresponding crystal faces should be in equally stable positions. Even though the total surface energy would decrease with an increase in the crystal size, according to the theory discussed no mechanism is available to accomplish such a change. The system may remain indefinitely in a state which is stable *with respect to other immediately attainable states*. Considering the critical importance of this experiment, one would like to see it repeated and confirmed by experiments involving annealing times longer than 6 min., and also with materials other than metals.

In their original paper, Harker and Parker made the additional assumption that polycrystalline metals, when annealed, will actually attain a grain boundary configuration stable in the above sense. From this assumption they derived the conclusion that, when a polycrystalline metal is annealed, grain growth eventually stops, as the stable grain boundary configuration is reached. Subsequent experimental work with high purity aluminum and with some high purity solid solutions[2] failed to confirm the cessation of grain growth in the postulated manner. In the present paper Burke shows that it is possible to accept the Harker-Parker mechanism of grain growth without the necessity of also accepting the assumption that a stable boundary configuration would be actually reached in the course of grain growth. As a matter of fact, experiments by C. S. Smith with soap foams, as well as the above mentioned results with high purity aluminum, indicate that the unstable boundary configuration is self-perpetuating. The stoppage of grain growth postulated by Harker and Parker may be considered very unlikely.

There are, however, other causes which may bring grain growth to a halt. The stoppage of grain growth by a dispersed second phase was observed long ago; it was first clearly described in 1916 by Z. Jeffries.[23] A great number of investigations dealt with the subject later. In recent isothermal studies at this Laboratory,[24] conditions were investigated under which an initial period of grain growth is followed by stoppage of grain growth as a result of the presence of a dispersed second phase in Al-Mn alloys. The stoppage of grain growth in commercial brass, observed by Walker, was confirmed and interpreted[25] in the light of these results as a second-phase effect. Burke's interpretation, in the present paper, of the inhibition effect found by Walker is in complete agreement with the interpretation referred to above.[24,25] An increase in the number of second phase particles increases the inhibiting effect which can then successfully oppose a higher level of "growth force"; consequently, grain growth stops at a smaller grain size.[24] The extreme sensitivity of the rate of growth, when the grain size is large, to even the smallest amounts of a second phase is clearly shown by the inhibition effects Burke found in high purity brass. Zener's interpretation as described in Burke's paper, of the inhibition by second phase particles as a surface tension effect is a notable contribution to the understanding of these phenomena.

That grain growth will cease, even in the absence of a second phase, when the grain size becomes commensurate with the specimen thickness, was shown for high purity aluminum.[22] The inhibition effect discussed above is, of course, by no means in contradiction with this specimen thickness effect. The two effects may occur independently in the same material, or they may overlap, according to the conditions. This is clearly shown by the data contained in Burke's Table 4. Under the heading "Equilibrium Grain Size"[*] the table gives the grain size values ultimately reached at various temperatures, with specimens of commercial brass of various thicknesses. If these ultimate grain size values are plotted for each temperature as a function of the specimen thickness (Fig 22), it becomes clear that, when the specimen thickness is very small, the ultimate grain size follows the straight line corresponding to the specimen thickness effect. Thus, in commercial brass, up to a specimen thickness of approximately 0.1 mm, where the grain size is limited solely by the specimen thickness, at 700 to 850°C the ultimate grain size is independent of the annealing temperature. On the other hand, at very large specimen thicknesses, the ultimate grain size is practically independent of the specimen thickness, but it is determined instead, by the inhibiting effect of the dispersed second phase. Under such conditions the ultimate grain size is strongly temperature-dependent. The data also indicate that between these two ranges there is considerable overlapping, so that in the intermediate range of specimen thicknesses both the specimen thickness and the inhibition by a second phase have some effect on the ultimate grain size. J. Towers Jr. at this laboratory observed similar behavior in high purity brass, except that for this material the thickness range in which the grain size is determined solely by the specimen thickness, is considerably larger. The effect of inhibition on the ultimate grain size at 800°C is not felt until a grain size of about 0.6 mm is reached.

The empirical formula Eq 7, proposed by Burke, does give a vanishing rate of growth when the grain size approaches its ultimate value, as is evident from the differential form, Eq 6. However, this formula suffers from two important disadvantages. First, it does not fit the facts and, secondly, it is not consistent within itself. As seen in Fig 23, where the dotted curves represent values computed from Eq 7, at both 700 and 800°C, there are rather large deviations between the grain sizes experimentally determined by Dr. Burke, and the calculated curves. The nature of the trouble is clear if one considers that the logarithmic expression in Eq 7 gives a gradual, asymptotic, approach to the ultimate grain size, which is only reached after an infinite time of annealing. The data obtained by Burke for 800°C are in accord with similar data obtained at this laboratory with Al-Mn alloys, in that the ultimate grain size is reached after a finite period of annealing. During a considerable part of this period the grain size increases according to the simple power law $D = K{\cdot}t^n$. After the period of initial grain growth, the grain size remains constant for long periods of further annealing, within the experimental accuracy of grain size determination. There appears to be in most cases only a relatively short interval of decreasing slope between the ascending and the horizontal straight line portions of the logarithmic grain growth lines (Fig 23). This rather sharp break in the curve, which is also shown by Burke's own experimental data in Fig 20, is not reproduced by his formula. The second objection to this formula is that it necessarily leads to a slope of 0.5 for grain sizes small in comparison with the ultimate grain size. (In order to make the initial slope apparent in the graph, the zero point of the time scale must be chosen to correspond with zero grain size.) As known from earlier work with high purity aluminum[22] and also from the present data on high purity brass, a slope of 0.5 is approached only with very high purity

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[*] In the physical sciences equilibrium designates states to which the system tends to return, when disturbed. In the present case the grain size will obviously not tend to return to the so-called "equilibrium grain size" if, by some means, a slightly larger grain size was reached. The term "ultimate grain size" had been proposed by Dean and Hudson,[26] in 1924; there does not appear to be any reason for changing this nomenclature.

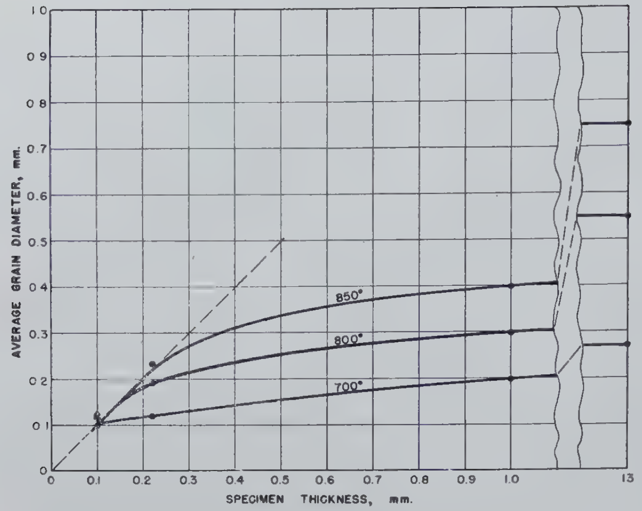

FIG 22—Ultimate grain size, D_n as a function of specimen thickness, for 70-30 brass of commercial purity, from data by J. E. Burke.

metals and solid solutions. In the presence of even small amounts of impurities forming a second phase, as in commercial brass, the initial slope becomes much smaller than 0.5. While the formula does, as intended, take into account the stoppage of grain growth after prolonged annealing periods as a result of a second phase, it represents the conditions during the period of initial grain growth as if no second phase particles were present. It is possible to devise empirical formulas, like the following one, which give considerably better approximation to the experimentally observed facts than Eq 7.

$$\log D = n.\log t - C\cdot t^m + K \qquad [9]$$

where n is the initial slope in accordance with the experimental data, parameters m and C are determined by the annealing time necessary to reach the ultimate grain size, and by the value of the ultimate grain size. The parameter K fixes the position of the initial ascending part of the grain growth line. This formula has the advantage of conforming to the simple power law to any extent required by the data. It has just the right number of parameters necessary to fit the data, and it reproduces the stoppage of grain growth after a finite time of annealing. Furthermore, the agreement is greatly improved by accepting the experimental fact that the ultimate grain size is temperature dependent, as discussed above. Fig 23 shows that the solid curves, calculated from Eq 9, fit Burke's experimental data for high purity brass at 700 and 800°C, considerably better than the formula proposed by him. In discussing his Eq 7, Burke introduces Eq 8 for the temperature dependence of his parameter K. However, he neglects the fact that D_f also varies with the temperature.

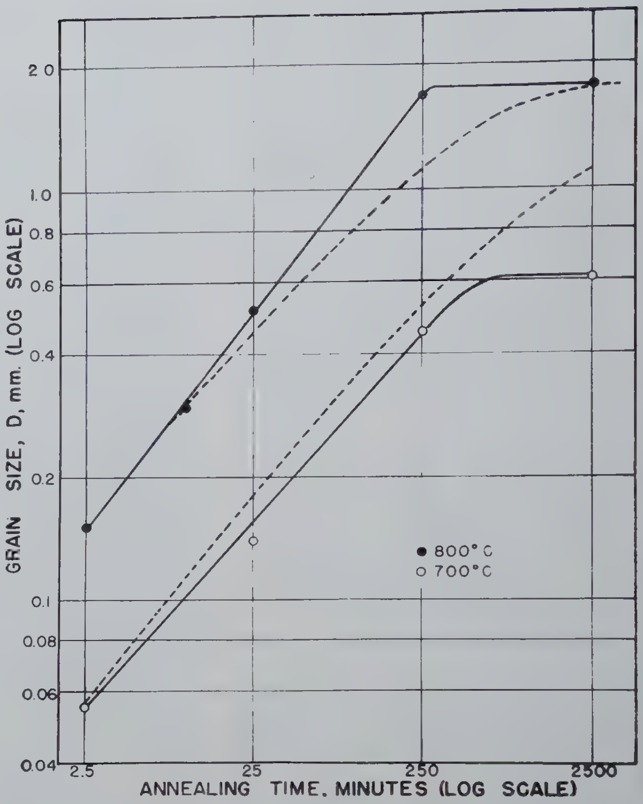

FIG 23—Comparison of grain growth data by J. E. Burke for high purity 70-30 brass with curves calculated from Burke's Eq 7 *(dotted lines)*, **and with curves calculated from Eq 9** *(solid lines)*.

In earlier publications[25,27] Burke proposed the following formula to take into account the initial grain size:

$$D - D_0 = K\cdot t^n$$

It has been shown[8] that this formula does not fit the data for either high purity aluminum or for brass. It is gratifying to note that in his present paper, Dr. Burke finally abandoned this formula and that he now uses the method proposed earlier in the work on aluminum,[22] to account for variations in the initial grain size.

It is a remarkable fact, discovered by Burke, that the slope of the logarithmic grain growth lines for high purity brass closely approximates the value of 0.5 over a rather wide temperature range. This value was previously derived[22] for high purity metals regardless of temperature. But in experiments with high purity aluminum the slope was found to increase with the temperature, and the theoretical value of 0.5 was approached only by extrapolation to the melting point. It was observed, however, that with high purity Al-Mg solid solutions n approaches the theoretical value of 0.5 at a lower temperature and then remains almost constant near that value.[29] The temperature range, within which n is nearly 0.5 increases with increasing Mg content. It may be that Cu-Zn solid solutions behave similarly. If so, one might expect that at relatively low temperatures the grain growth line for high purity brass containing lower amounts of zinc, such as 5 or 10 pct, would have a temperature dependent slope, lower than 0.5, but that, beginning with a certain temperature, the slope would approximate 0.5, and become independent of temperature. This temperature would then decrease with increasing Zn content, until it would fall below 500 or 450°C for 70–30 brass.

Burke gives a heat of activation value for grain growth in high purity brass (40 K cal per g atom), which is considerably lower than the value previously found by Burke and confirmed at this laboratory for commercial brass (60 K cal per g atom) in the range between 450 and 700°C. In the course of work with high purity brass done by John Towers, Jr. at this laboratory, using laborious and very careful grain counting techniques and a larger number of specimens, a value distinctly higher than that reported by Burke, namely 49.8 K cal per g atom, was obtained. When Dr. Burke's data were used to calculate a heat of activation from the time to reach a grain size of 0.1 mm, it was found by Mr. Towers that a value of approximately 46.5 K cal per g atom fits the data best. This is in better agreement with the above value, calculated by Towers from his own data, than the 40 K cal per g atom value given by Burke.

J. E. BURKE (author's reply)—In reply to Mr. Wensch, I believe the apparent migration of a boundary away from its center of curvature can be explained. C. S. Smith has pointed out that a surface may be curved about two axes at right angles to each other so that the net curvature at any point on the surface is zero. The surface is thus equivalent to a plane and will have no tendency to migrate. A plane will intersect such a surface in a curved line, however. Thus, on a plane polished surface of a metal specimen, it would be impossible to differentiate between it and a truly curved boundary which should migrate toward its apparent center of curvature, or even one which should migrate away from its apparent center of curvature. Any studies of grain growth on a polished surface are open to some doubt, also. A grain which intersects a surface has a different environment from a grain in the body of a specimen. Grain boundaries will intersect the surface at 90° at equilibrium, and an intersection at an angle of other than 90° may lead to grain boundary migration to readjust the angle. In reply to Mr. Wensch's second question, the quantity D which appears in Eq 3 is the same as the quantity D_f in Eq 7.

As Dr. Dunn has beautifully shown at this meeting, the surface tension of the grain boundaries does depend upon the relative orientation of the grains on opposite sides of the boundaries, and thus only rarely will the equilibrium boundary angle be precisely 120°, as called for on a simple, isotropic surface tension picture.

I agree with Dr. Gulbransen's concern about the physical significance of the activation energies presented in Eq 2 and 8. The value of 40,000 cal per mol (rather than 60,000 cal per mol for commercial purity brass) for high purity brass is very close to the reported heats of activation for diffusion of zinc in brass of that composition. One is thus tempted to suggest that grain boundary migration occurs by a diffusion mechanism. Against this is the uncertainty of the mechanism of grain boundary migration, and the fact that a change in number of inclusions with temperature may influence the temperature dependence of growth rate and the computed value of H. Later evidence which will be published shortly indicates that the temperature dependence of the rate of grain boundary migration in pure copper varies with the crystallographic direction of boundary migration. Since diffusion in cubic metals is isotropic, this indicates that grain boundary migration is not identical with bulk diffusion. However, in a two component alloy like brass, there may well be an adsorbed layer of zinc at the grain boundaries, so that this must migrate by lattice diffusion when the grain boundary migrates by any other mechanism. This could well be the rate controlling step, and thus one would measure the activation energy for diffusion of zinc.

Mr. Beck's discussion is exhaustive, and in the interest of brevity I shall answer only those points which are pertinent to this paper and not already discussed in the body of the paper.

As was stated, a number of workers have postulated that surface energy is the driving force for grain growth, but contrary to Mr. Beck's statement, by no means all workers have accepted this explanation. In any case, it is preferable to use experiment rather than acceptance by workers in the field to test the validity of an hypothesis. The concept that the escaping tendency from a surface is a function of the curvature of the surface is not new. W. Thomson[30] showed that the vapor pressure of a liquid droplet is inversely proportional to its radius of curvature, and the formal proof of this may be found in most texts on Thermodynamics.[31] Vogel and Harker and Parker applied this concept qualitatively to the migration of grain boundaries, and in the present paper it has been applied quantitatively.

It takes energy to create a new surface, therefore a small crystal, which has more surface per unit volume than a large crystal, will have more energy per atom than a large one. In solution where there is a constant interchange between surface atoms of the crystal and saturated solution, there will be a tendency for large crystals to grow at the expense of small ones. For this effect to result in an appreciable rate of growth, however, the small crystals must be very small, much smaller than the grain sizes in metals where grain growth is experimentally observed to occur at measurable rates. There is undoubtedly a slight tendency for a large grain to grow at the expense of a small one in a solid metal, across a plane interface, but the effect is so small that it is not observable, as evidenced by the fact that plane grain boundaries between grains of different length along a wire do not migrate. The greater stability of a plane surface over a curved surface is shown by the restoration of a fragment of a crystal into an ideomorphic crystal when the fragment is immersed in a saturated solution. The solubility of the curved faces and edges produced by fracturing is greater than the solubility of the perfect crystal. In polycrystalline metals the relatively rapid rate of grain boundary migration results from a convex surface (positive curvature) being in contact with a concave surface (negative curvature). The difference in escaping tendency between these two surfaces is much greater than the difference between two surfaces having similar curvatures of the same sign. As was explained in the paper, this accounts for the very low rates of grain growth in partially melted specimens. Nevertheless, if they were heated for very long periods, one would expect small amounts of growth of the large crystals to occur at the expense of small ones.

Mr. Beck concurs with the statement in the paper that it is unlikely that grain growth will stop by the grain shapes fulfilling the Harker and Parker criterion for equilibrium, and quotes evidence from his own work that grain growth does not stop. One of the objects of this research was to reconcile the indication of his work that grain growth continues at an unabated rate until the grain size approximates the size of the specimen, with the fact mentioned by Mr. Wensch that grain growth frequently stops earlier than this. I am glad Mr. Beck now agrees that grain growth does not necessarily continue until the grain size approximates the size of the piece, and regret that his explanation of the phenomenon was not available until some time after this paper was submitted for publication. It is somewhat surprising that he agrees with the Zener formulation of the inhibiting effect of second phase particles, since it also is based on the assumption that grain boundary curvature is necessary for grain growth to occur.

As Mr. Beck mentions, the specimen thickness effect is by no means in contradiction to the inhibiting effect of inclusions, rather, as is explained in the paper, they are different manifestations of the importance of grain boundary curvature.

It is not clear what Mr. Beck intends to show by Fig 22. The data on specimen thickness were used in the paper to show that in very thin specimens the limiting grain size was a larger proportion of the specimen thickness than in thicker specimens, because in thin specimens the grain size is smaller and thus the growth force is greater. The results thus confirm the explanation given for the specimen thickness effect.

Mr. Beck objects to Eq 7 and has presented an empirical four constant equation which fits the experimental data better. It is agreed that there are numerous mathematical procedures for fitting a curve to a set of data, determining the equation for the curve, and evaluating the constants in the equation. The object in presenting Eq 7 was not to develop an empirical equation which would fit the data obtained, but to test the assumptions made as to the mechanism of grain growth. These assumptions were that the rate of growth is proportional to the effective curvature of the boundary, that is the difference between the present and the limiting curvature, and that the effect of temperature is to vary the specific reaction rate constant, K, according to the Arrhenius relationship

$$K = A \cdot e^{-H/RT}$$

The equation is semi-empirical, in that the constants K and H must be evaluated experimentally. The slopes of the curves, and the general shape are not controlled by arbitrary constants as in the equation proposed by Mr. Beck. When the mechanism of the process is better understood, it should be possible to compute the value of H and K, and in principle, even D_f. For example, factors which will influence K are the surface energy of the boundary, and a geometric factor relating the rate of grain growth to the true rate of grain boundary migration. It is also obvious that if the temperature dependence of D_f had been taken into account a better agreement with the observed data would have been obtained. This has been stated elsewhere.[32] The quite good agreement between the curves calculated from these assumptions and the observed data are taken to indicate, as stated in the paper, that these assumptions are essentially correct.

It should be pointed out that the earlier derivation of the slope of 0.5 for the log grain size versus log time curves[5] was based upon the assumption that the rate of grain growth is proportional to the total amount of grain boundary present. The present hypothesis is that the rate of growth is proportional to the effective curvature of the grain faces. It possesses the advantage that the role of inclusions and changes in grain size distribution can be explained on this basis. Only in the absence of inclusions and only when the relative grain size distribution remains constant does the present assumption lead to a slope of 0.5 for the logarithmic curves.

The earlier heat of activation of 60,000 cal per mol (based on Walker's work, and confirmed by Beck) was shown in the present work to be influenced by solution of impurities as the temperature increases. The value of 40,000 to 43,000 cal per mol observed for the high purity brass in the present work is at least internally consistent at all temperatures. In recomputing a value from the present data, Mr. Towers has taken as his measure of rate the time necessary to reach a grain size of 0.1 mm, and presumably measured his own value of 49.8 K cal per mol in a similar way. This method of comparing rates at different temperatures is less certain than the method of superimposing curves, since the curves must be extrapolated and there is considerable freedom in selecting the exact slope to the extrapolated. When the curves are superimposed, more of the data can be used.

It is felt that it is meaningless to give such activation energies to three significant figures, for several reasons:

1. The rate of grain growth (rate of disappearance of grains) is not the fundamental process for which an activation energy should be computed. The fundamental process is the migration of grain boundaries, and one must assume that the rate of grain boundary migration is proportional to the rate at which grains disappear.
2. There may be reasons other than a change in the number of activated atoms with temperature which cause the rate of grain growth to change with temperature. An example cited in the present paper is a change in the number of inclusions. Another possible one is a change in the mechanism of grain boundary migration.
3. Later work indicates that the activation energy for grain growth depends upon crystallographic factors, and that it may differ for different directions of migration of the same grain in a uniform matrix. Thus at best an average value will be measured in a polycrystalline material, and it might change with differences in preferred orientation.

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Preferred Orientation in Rolled and Recrystallized Beryllium

By A. SMIGELSKAS and C. S. BARRETT

DISCUSSION

(*E. Parker presiding*)

J. T. NORTON*—I think Mrs. Smigelskas Fischer has done a splendid job in working out the pole figures from rather difficult photograms which are common to beryllium. Is there not a mistake in Fig 2 in that the pole figures B and C have been interchanged?

A. SMIGELSKAS FISCHER (authors' reply)—Yes, there is such an error in the labeling of the pole figures of Fig 2. The correct plane for Fig 2b and 2c is the plane in parenthesis above the figure numbers and not that in the figure subtitle.

J. T. NORTON—Also, I would like to mention another method of obtaining the data for pole figures which would be particularly applicable to this problem. It is a method which has been published only recently and some of you may not be familiar with it. In the use of thin foils, such as are involved in this problem, it again involves making up a sandwich out of several sheets cemented together with the rolling direction parallel in all sheets and then cutting out small cylindrical rods just as Mrs. Fischer did. Several rods would be cut out of the specimen with their axes making various angles with the rolling direction. These rods are then put in an X ray spectrometer fitted with a Geiger counter tube and the intensity of reflection from a particular family of planes is recorded as the rod slowly rotates. For instance, if we were to make a basal plane pole figure corresponding to Fig 2 of the paper, the cylindrical rod with its axis parallel to the rolling direction would be mounted in the direct beam of the spectrometer with the rod axis parallel to the spectrometer axis. The Geiger tube would be set at the correct angle to receive the basal plane reflection and clamped. The rod is then rotated at a constant rate and the output of the Geiger tube recorded on the chart. The resulting curve represents the intensity variation and hence the pole density variation for a diameter of the pole figure perpendicular to the rolling direction. Similarly, each of the other rods will give information about other diameters of the pole figure. Since the rods are geometrically identical, no absorption correction is necessary and all of the curves will be consistent. By drawing lines at different intensity levels above the background and measuring the angles at which these lines intersect the curves, data are available for drawing accurate pole density contours on the final pole figure. Usually six rods are sufficient to give adequate coverage of the pole figure and no part of the figure is left out. For a material as transparent as beryllium, the rods could be made fairly large and since a considerable length of the rod can be illuminated, a good integration is obtained for fairly coarse grained materials.*

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* Massachusetts Institute of Technology.

A. SMIGELSKAS FISCHER—Thank you very much for describing your method. It seems to be more effective than the one we have used inasmuch as it enables one to obtain quantitatively the variation of intensity of scatter about a mean which is important in determining the exact extent of preferred orientations. We were able to estimate this extent only by eye. However, this work, which was declassified only recently, was completed several years ago. At that time, we did not have the benefit of your nice technique nor a spectrometer with which to develop any similar method.

E. PARKER*—Everything sounds so easy the way you described it in the figures. I once tried to roll some beryllium. That was not so easy; in fact we found it very difficult. Would you care to make some comments about how the beryllium was rolled?

A. SMIGELSKAS FISCHER—I am sorry, but that is still classified information,

E. A. GULBRANSEN†—Could you use any other radiation instead of molybdenum?

A. SMIGELSKAS FISCHER—We could use other radiation but we found molybdenum best suited for our purposes.

E. A. GULBRANSEN—Though with a small figure?

A. SMIGELSKAS FISCHER—Even though the figure is small the lines are sharp and we are able to differentiate between the diffraction rings. While using longer wave lengths would spread the figure, it would also tend to broaden the lines and weaken their intensity if the same specimen to film distance and the same exposure time were used. Therefore, we felt that we would not gain any advantage from a larger figure.

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* J. T. Norton: *Jnl. of Appl. Phys.* Dec. 1948, 19, 1176.

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A Study of Textures and Earing Behavior of Cold-rolled (87-89 pct) and Annealed Copper Strips

By MING-KAO YEN

DISCUSSION

(*S. E. Maddigan presiding*)

S. E. MADDIGAN*—I think Mr. Yen should be complimented on doing a very excellent and a very comprehensive piece of work. I was particularly pleased to note the use of X rays in a somewhat less tedious technique than pole figures. In the past I think many workers have been diverted away from the use of X rays in such investigations because of the large amount of work involved in pole figures if one is dealing with a great number of specimens. The same thing, I think, applies to the determination of orientations by counting of twins which is also a very tedious procedure; as a result several papers which have otherwise been of excellent quality have depended upon etching techniques for determination of orientation. The present paper indicates that the results reported in those previous papers were correct, but I think the use of etching techniques alone is a rather shaky basis for setting up theories in the literature.

W. M. BALDWIN, JR.*—This discussion will be a short note of correction and apology. In my discussion of Brick, Martin and Angier's paper I incorrectly reported the orientation of phosphorus deoxidized copper annealed at temperatures. When I learned that Mr. Yen was preparing the present paper I asked that he correct this previous error, which he most graciously consented to do. However, through my ambiguity the correction noted on p. 59 of Mr. Yen's paper is still not the proper one. For this I take full responsibility. The orientation which I observed in phosphorus deoxidized copper at high temperatures is the (112) [11$\bar{1}$] which agrees with the pole figure given in Fig 8a, on p. 65 of Mr. Yen's paper. Our observations were made on the basis of twin counts rather than X ray determinations and therefore serve as an independent confirmation of Mr. Yen's data.

M. K. YEN (author's reply)—The author wishes to thank Dr. Maddigan for his comments in regard to the application of glancing technique to textures. As a matter of fact, considerable work has been done recently in connection with the study of rolling, wire drawing and electrolytic deposition textures for copper and its alloys by this method or some modification of it. It is to be expected that this technique may be developed to its full practical importance. In the case of copper, it was found that the approximate position and relative height of ears in deep drawn cups, as well as grain size and degree of recrystallization, can generally be derived from a single X ray glancing photogram.

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Pressure Distribution in Compacting Metal Powders

By POL DUWEZ and LEO ZWELL

DISCUSSION

(*L. S. Busch presiding*)

L. S. BUSCH*—A very interesting use of a new engineering material, the strain gauge, is, I believe, one of the first as applied to powder metallurgy.

J. WULFF†—We have here another valuable contribution to the fundamental data on powder metallurgy from Professor Duwez's laboratory at California Institute of Technology. I am particularly pleased with the measurements which relate to the vertical pressures but not with the measurements which relate to radial pressures on the die wall. In regard to the latter, we gave up similar attempts in our own laboratory to measure radial pressures by methods similar to those used by the authors of this paper since we believed that their very method of measurement would introduce appreciable error. For this reason, one of my coworkers, Dr. Shank, studied the pressure on the die wall by using a cylindrical thick-walled die with a goodly number of closely spaced strain gauges on the outer wall. The strain distribution in the die wall was thus obtained during pressing from both sides. This enabled the determination of both frictional and radial forces acting on the die wall. The distribution of radial forces in this work appears to be quite different from that obtained by Duwez and Zwell.

A. J. SHALER*—I am very glad that we now have some stress distribution data on the bottom plunger of a cylindrical die during pressing. These data, along with the side-wall pressure data which the authors have given, and which have also been obtained by the method just described complete the elements required to solve the entire stress strain problem in cylindrical compacts. In previous years Kamm, Steinberg and Wulff have solved the strain distribution problem. I wonder if Professor Duwez could be induced some time when he is not too busy to put some of his strain gauges in the top plunger as well. It would not be necessary, I think, to have the top plunger stress distribution in order to solve the entire problem, but these data would certainly provide a very useful check on the result.

P. DUWEZ (authors' reply)—I think those experiments could be done very easily by using a floating die and two moving plungers instead of one.

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Lead-grid Study of Metal Powder Compaction

By R. KAMM, M. A. STEINBERG, and J. WULFF

DISCUSSION

(*L. S. Busch presiding*)

L. S. BUSCH*—We have had presented two methods of measuring these variations in powder compacts.

E. OROWAN†—In connection with the rolling mill research work carried out at the Cavendish Laboratory, Cambridge, with the help of the British Iron and Steel Research Association, Dr. E. A. W. Hoff, Mr. J. Los, and myself, have determined coefficients of friction at extreme pressures for a number of liquid and solid lubricants, both by direct measurement, and by calculation from measured values of the roll force. The most efficient lubricants at these high pressures (for the small amounts of sliding that occur in rolling) were camphor and, in particular, borneol (Borneo-camphor). Perhaps such lubricants could be used with advantage in the kind of work described by Dr. Wulff.

L. S. BUSCH—I think Dr. Wulff has in the past mentioned experiments which have been performed in the extrusion and rolling of metals and which led to conclusions which can be applied to the compacting of metal powder.

A. SQUIRE*—There have been some recent developments in the field of high pressure lubricants which indicate that boron nitride might be a very desirable material to employ as a die lubricant. At the present time its cost is prohibitive, but as the need arises for the material it will undoubtedly come down in price. The present price is $200. a pound.

It is my understanding that one of the reasons for vacuum pressing both in ceramics and metal powders, is to prevent the formation of what we call pressure cracks on ejection. I have been assured by people who have done the work themselves in the field that it is possible to press powders at considerably higher pressures under vacuum than it is in air. Apparently the gases trapped during the pressing operation add sufficiently to the internal stress in the compact so that these pressure cracks are formed on ejection. In vacuum pressing this can be avoided.

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L. S. BUSCH—I feel that Mr. Squire has a good point, but I also feel that there is another factor as far as pressure cracks are concerned and that is simple expansion as the piece comes out of the dye.

J. WULFF (author's reply)—We have not tried the borneol (Borneo-camphor) suggested by Dr. Orowan. The extremely high point pressures met with in pressing lead us to believe that it should be applicable.

In answer to Mr. Squire, we have found that boron nitride behaves as an abrasive and not as a lubricant in powder pressing. Its application to the lips of crucibles, since it is difficult to wet by molten metal, suggested its use. In an auxiliary research it was also used as a constituent of powder metallurgy bronzes which were tested for friction and wear. No reduction in friction or wear was experienced. Indeed rolling boron-nitride torn loose from the compact accelerated the wear appreciably.

In regard to Mr. Squire's remarks on pressing, I must say that entrapped air can lead to fracture of the compact as it is ejected from the die or later during sintering. Our results indicate nevertheless that nothing is gained from a density standpoint by vacuum pressing of hard powders and little with soft powders that cannot be achieved readily by efficient lubrication.

Perhaps Professor Shaler would care to comment on Mr. Busch's remarks.

A. J. SHALER*—We have found that cracking upon ejection of the compact is not always due to the lateral elastic expansion of the compact as it comes out of the die, but must occur as soon as the pressure is released. The pattern of stresses set up in the compact when the load is removed from the die walls is such that cracks may form at the center of the compact and spread upward laterally outwards. The way to avoid cracks of this kind would not be to increase or decrease the pressure or change the lubricant, but simply to build dies of greater rigidity so that a lesser residual-stress pattern is created when the die walls push back on the compact elastically after release of the pressure.

J. CORDIANO*—On the subject of pressure cracks in specimens on ejection from dies one of the simplest ways of preventing such cracks is to maintain a partial top pressure on the compact during ejection. One question I wanted to ask Dr. Wulff regarding pressing and sintering of these copper compacts is whether he noted bloating of the sintered specimens which were pressed at 60 tsi. Also, was there any difference in bloating tendencies when sintering in vacuum or hydrogen?

J. WULFF—The present tests on copper were sintered in a dilatometer set-up which did not permit close observation of the compact surface during sintering. I have, however, noticed the "bloating" mentioned by Mr. Cordiano on copper compacts pressed at pressure above 60 tsi and later sintered in hydrogen. Indeed, some of these specimens have even exploded in the furnace. Mr. Cordiano's remark that pressure cracks can be avoided by maintaining some pressure on the compact during ejection is well taken. S. K. Wellman has long advocated this technique in the pressing of thin specimens of large area.

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Properties of Chromium Boride and Sintered Chromium Boride

By S. J. SINDEBAND

DISCUSSION

(E. Parker presiding)

J. WULFF*—It seems to me that the author could improve the quality of his high temperature material by using less nickel as a cementing agent in hot pressing. Furthermore, to avoid the presence of undiffused nickel which would not be oxidation resistant, permit me to suggest that he use a nickel-chromium powder containing a small percentage of boron. This would give him a liquid phase at a lower temperature and accelerate both sintering and homogenization. The commercial alloy known as colmonoy contains sufficient chromium to be heat resistant and sufficient boron to be of low melting point. Such an alloy may be applicable as a cementing agent in increasing the quality of Mr. Sindeband's alloys. Finally I believe the author unfair to himself in expecting a porous material to have properties equivalent to one of 100 pct density.

S. J. SINDEBAND—Dr. Wulff's point is well taken. Early in the program we realized the fact that we were having difficulty with these low-melting alloys, and we had hoped, since the colmonoy alloys of which you speak are at the nickel-rich end of the diagram, that by going to the other end of the diagram (chromium boride-rich) we would not have this difficulty. Thus we tried to use very small percentages of binder; but for reasons which are not exactly apparent we found that when we did this it was necessary to raise the pressing temperature to a point which we were unable to attain. For all compositions which we tried using nickel, or for that matter any nickel iron or cobalt containing material as a binder, we found that we would get low melting boride phases, which as you point out are the commercial "strength" of the hard-facing materials. I personally believe these owe a great deal of their behavior and even hardness to the nickel boride which is considerable evidence when an alloy of chromium boride is made with nickel. Nickel boride itself is very hard. We did try pure chromium as a binder and found there was considerable difficulty in handling it, particularly since we could not just hot press under the atmosphere conditions obtaining there. We found that when we vacuum sintered chromium boride, we developed extremely brittle materials, and had to abandon that. It looked quite fruitful at one time. We attempted to make use of materials which either did not form known borides or which formed refractory borides and used those as binders. Apparently the chromium boride itself enters into entirely too many side reactions with binders to permit us to make use of chromium boride to get the ultimate result we were seeking in this particular field.

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The comparison with vitallium is a cruel one, but nevertheless it is one which I chose to make simply to indicate the goal for which we are aiming. I believe that alloys of this variety will be able to achieve high temperature strength equivalent with materials such as vitallium and better than that. What we need to do is to find if we continue with borides, a material which does not lose its boron to the binder phase but which will enter into a cementing action with the cement chosen which is similar to that observed in the case of carbides. There actual re-precipitation occurs and much of their strength comes from the matrix and not from the binder.

W. J. KROLL*—It would be of interest to know how much oxygen the powdered chromium boride contained, as well as how much oxygen was present in the chromium powder used for sintering. Wet grinding of such active metals or alloys introduces large amounts of oxide and the contaminated materials may not bind in the sintering operation.

S. J. SINDEBAND—We spent a good deal of time attempting to determine the oxygen content of the boride. Unfortunately the oxygen was largely tied up in the form of oxides of the aluminum which was used for the reduction of the original oxides in thermite reduction, and as such we met great difficulty in making any determination. It was not too clear whether it was all tied up as aluminum oxide or as some complex silicates. However, the analysis of the powders indicated that there was an unaccounted for amount, I believe, of about 3 pct. The table directly under the X ray patterns indicated, for the thermite process, that the known elements added up to 97.25. How much oxygen was in that residue we could not know. As far as the chromium is concerned, we found standard electrolytic chromium unsatisfactory as a binder with which to press the powders. The procedure that we used was to purify this chromium powder by a reduction in extremely dry hydrogen. We found that if we got the dew point down to the temperature of liquid air we could bright anneal the chromium powder and come out with a powder considerably more ductile. We were then able to press good compacts, but still the resulting sintered cold pressed products were very brittle. The transverse rupture strength was of the order of 27,000 to 30,000 psi, or perhaps a shade higher.

MEMBER—I am particularly interested in the field of wear resistance, and I wonder whether the author has done any work or considered any work in studying these chromium boride compacts as wear resistant materials. You have shown that you had some difficulties in making the high temperature resistant material, but this might be very good wear resistant material.

S. J. SINDEBAND—We have not made any actual wear resistance tests. I believe the wear resistance of this material could be assessed on the basis of the properties that have been presented. Hardness is of major importance. The toughness of the material would be indicated by its transverse rupture strength. I believe that material of this composition has been given some use in cast form by the Wall-Colmonoy people. I would expect that this material as hot pressed would be able to do anything that that material could do, and perhaps do it better by virtue of the finer structure which is attained in this material, much the same as you would expect to get in a comparison between a cast carbide versus a cemented carbide. The wear resistance, I think, of these materials should be good. I think it would depend entirely on the actual application. If there is any acid corrosion present under the circumstances under which you want wear resistance, I think this is a very good material. We did try it as a tool material just briefly, and it cuts well. Actually I believe that if you have anything of 89 or so Rockwell hardness and a transverse rupture strength above 100,000, you can cut and cut well with it. That is good enough, I feel sure.

A. SQUIRE*—I may be mistaken but in looking at that micrograph presented in the paper it seems to me the particles are larger than 3 to 5 microns. The micrograph looks similar to those of carbide where the particle size is possibly one to two microns. Did that micrograph show that much particle size or did the grains grow?

S. J. SINDEBAND—The 3 to 5 micron particle size was the starting point. We did observe with this material the grain growth was obtained in the hot pressing operation.

R. KIESSLING*—Binary systems, composed of a transition element and boron have been studied for four years at the Institute of Chemistry, University of Upsala. The chromium-boron system belongs to those which have been investigated. As the results in some instances are different from those published in this paper, a short note may be of interest. (The results have been received by *Acta Chemica Scandinavica* for publication.)

Five intermediary phases have been found with relatively small homogeneity ranges and boron contents of 33 (δ), 40 (ϵ), 50 (ζ), 55 (φ), and 67 (θ) at. pct. The structure of the η-phase has been mentioned in connection with a report on the system zirconium-boron (*Acta Chem. Scand.* (1949) **3,** 90). The structure of the ϵ-phase is in accordance with the data given by Mr. Frueh. The position of the boron atoms has been determined using Fourier methods. The boron atoms form parallel chains through the metal lattice. The structure is closely related to the structures of the δ-phase in the systems molybdenum and tungsten-boron. (*Acta Chem. Scand.* (1947) **1,** 893).

The system behaves in accordance with Hägg's rule for a content of boron up to 60 at. pct and is more complicated than the systems molybdenum-boron and tungsten-boron. The latter two systems have the radius ratio closer to the critical value. The system zirconium-boron, with a radius ratio on the other side of this value has only one simple intermediary phase.

S. J. SINDEBAND—I was very interested to note that work is continuing on a broad scale on the binary systems with boron, at the University of Upsala; particularly since so much of interest emanated from that institution in this field in the past.

I was particularly interested to find that Dr. Kiessling had made an extensive study of the chromium boron system and that his data for the structure of the phase around 50 at. pct corresponded with the data given in the paper I presented, as obtained by Mr. Frueh. In none of the X ray investigations made on chromium boride did we note lines which would correspond with the other bordering phases he has reported. It is quite possible that the method by which the material is made has something to do with this.

I shall await with interest the publication of the complete data regarding these phases.

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Solubility Relationships of the Refractory Monocarbides

By J. T. NORTON and A. L. MOWRY

DISCUSSION

(*E. Parker presiding*)

W. J. KROLL*—I think that since oxygen and nitrogen have a tremendous influence on the mechanical properties of these metals, it can be expected that tracers might have also considerable influence on the mechanical properties of these carbides, I wonder also how far residual oxygen and nitrogen may interfere with the determination of your lattice constants.

J. T. NORTON (authors' reply)—Thank you, Dr. Kroll, for bringing up this question about which we have thought a good deal. We have no specific analysis for oxygen on these carbides chiefly because I do not know how to do it. Maybe you have a suggestion. We do know however that in comparing careful measurements of lattice parameters of the carbides which are deficient in carbon, and where the carbon is undoubtedly replaced by oxygen or nitrogen or both, there is a negligible change in the value of the lattice parameter until there is a very considerable deficiency in carbon. Titanium carbide is the one we have investigated most completely, and until about a quarter of the possible carbon atoms had been removed there was very little change in the parameter, but beyond that it drops very rapidly. It is believed titanium oxide, TiO and TiC can form a continuous series of solids. It has been investigated but the lattice parameter curve is not linear, and is almost flat at the carbon rich end. Our investigation is based on the carbides which are very nearly saturated with carbon. I am inclined to believe that these impurities which are undoubtedly present in our carbides have very little influence on the lattice parameter because both nitrogen and oxygen will replace carbon in these monocarbides atom for atom. If we had a good method for analyzing for oxygen we would feel a lot better about results of this type. Mr. Redmond of Kenemetal Corporation has offered to provide us with some carbides made by Mr. Mackenna's process, the so-called Menstruum process you mentioned. It would be interesting to see if those carbides give any different results from the ones which we used.

J. WULFF*—Many of us peruse the literature of powder metallurgy and have been taught that double carbides of refractory metals can be made by the Menstruum method. Are we to believe from the work of the above authors that double carbides cannot be made by the Menstruum method?

J. T. NORTON—You put me on the spot. Certainly in the binary systems, which we have investigated here, there is no evidence of the formation of a double carbide. These are simple replacement solid solutions. There is no critical composition and there is only one type of structure observable over the whole range of compositions.

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The Magnetic Properties of Sintered Iron and Iron Base Alloys

By W. ROSTOKER

DISCUSSION

(*A. Squire presiding*)

S. J. SINDEBAND*—(1) Discussing the properties of the powders used, Mr. Rostoker mentioned a silicon powder as being between 150 and 325 mesh. We always had much difficulty in measuring particle size of silicon powder by screen analysis, because of its tendency to agglomerate. I would be interested in the method used to measure these particle sizes.

(2) Mr. Rostoker maintains that the measurement of magnetic properties is more accurate in determining complete homogenization of an alloy, than is the X-ray diffraction technique. I wonder whether this is really true. Even when diffusion is complete, magnetic properties will change during continuation of the heat treatment, due to change in density and pore shapes, as has been demonstrated by Mr. Rostoker himself. Which effect is faster, the diffusion of the alloy components or the attainment of final density, will, in my opinion, depend very much on initial material and sintering conditions used. For magnetic applications, of course, the magnetic measurements are most suited for determining the point at which equilibrium conditions are reached.

(3) I was glad to see that Mr. Rostoker had used sample sizes which are similar to those I had used previously, and I believe that ring samples of about 2 in. od will become more or less standard samples for the determination of magnetic properties of powder metallurgy products. I should like to ask how the density was changed for the samples on which the effect of porosity was investigated, and, further, why the sintering temperature used for this series of experiments was so low. It is somewhat surprising that a 24-hr treatment at 850°C acts so much more to spheroidize the pores than a treatment for 1 hr at 1100°C. But the effect seems to be indisputable. I have made an investigation of the influence of sintering temperature for longer times on the maximum permeabilities of iron powder compacts which was presented at the International Powder Metallurgy Conference in Graz, in 1948, and I hope that these results will be published here within a short time. The results of this investigation are confirmed by Mr. Rostoker's findings that the change of time from 1 to 24 hr changes the permeability behavior considerably in the direction as indicated by Polder and Van Santen for spheroidization of pores. I do not quite understand Mr. Rostoker's explanation of the influ-

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ence of "high" and "low" permeabilities on the shape of the curves for induction vs. density. Even for the large fields ($H = 100$), the permeability is still in the neighborhood of 100, that is, it is equal to the largest value Polder and Van Santen have used. I believe the fact that the permeability is not constant will make a refinement of Polder and Van Santen's theory necessary, though the general trend for flat and spherical pore shapes will probably be maintained.

(4) The densities obtained for any alloy material produced by Mr. Rostoker are rather low if compared with his excellent values for pure iron. This has to be expected, but points in the direction mentioned above, that homogenization is not necessarily connected with constant magnetic properties. An attempt to study diffusion in Fe-Si alloys by resistivity measurements was recently published by F. W. Glaser in the "Powder Metallurgy Bulletin." We are now studying the ferrosilicon materials over the full range of alloys, especially as far as resistivities and magnetic properties are concerned, and hope to publish something about these compositions within this year. Mr. Rostoker reports about a so-called anomaly in his Fe-Ni alloys with regard to the maximum permeabilities. These are inferior to data published in the literature, while, for instance, B_{100} and H_c are very close. In my opinion, the explanation for this behavior is the porosity of the alloys, as they are at the best 95 pct dense. Saturation and coercive force are much less sensitive to the influence of porosity than is maximum permeability. This might also give an explanation why there was no influence of nitrogen noticed in Fe-Co alloys, where the maximum density is still lower. The investigation by Mr. Rostoker, about the differences in properties obtainable by sintering in hydrogen or cracked ammonia, was especially interesting and might explain a number of discrepancies so far reported in the literature.

F. W. GLASER*—With regard to the preparation of the Fe-Si compacts, though not mentioned, I assume that Mr. Rostoker has mixed the Si and Fe powders by a tumbling operation. In view of the difference in density of these two powders, I myself have experienced great difficulty in obtaining the desired overall Si percentage, as it was theoretically calculated. Further, I wonder whether chemical analyses were run on the Fe-Si compacts reported. The exact overall Si content of the range of Si alloys reported in Mr. Rostoker's paper is extremely important, since as little as 0.25 pct Si in this region has quite an influence on the electrical resistivity. I should like to know to what extent Mr. Rostoker was sure that the Si percentages were really of the reported compositions.

F. N. RHINES*—I would like to say a few words in defense of the X ray method. I suppose that everyone who has thought about the problem of measuring homogenization in powdered compacts has thought of using the X ray method, and each person, in turn, seems to have become discouraged with it, but there is a basic advantage in its use, and I think we should not lose sight of it. Apparently, the thing that Mr. Rostoker has done has been simply to measure the position of maximum intensity in the reflection that he chose as his index and to watch the progress of that point of maximum intensity during heat treatment. It is fairly evident, and I think every one who has done this work has observed, that there is another phenomenon that takes place at the same time. The line first broadens so that it covers all of the parameter values from that of the pure solvent to that of the saturated solid solution. The broadened line first shows its maximum intensity somewhere near that of the pure substance; then, as time goes on, the maximum intensity shifts and, after the maximum intensity reaches somewhere near the point where it will stabilize in parameter value, the breadth of the line decreases, that is, the line becomes progressively sharper.

Now, if we could make good intensity measurements across the line we should have an index not only of the average change in composition of the material during homogenization but a detailed description of how much of each composition is present at any given time during the homogenization process. This information would be invaluable in making a complete statement of the state of homogenization at any period.

We cannot get that kind of information from any measurement which gives us only an over-all average figure, therefore it seems to me that in the long run it would be highly desirable to get the X ray method under full control and to use it for this type of research.

J. T. NORTON†—I do not believe that the X ray experiments described in this paper really indicate what the X ray method is capable of doing. A change in parameter is not a very sensitive measure of composition. As I understand this problem, it is one of determining whether or not a sample is of uniform composition; certainly the measurements of the line broadening would be much more sensitive. This is true provided the work on line broadening is carried out properly, and it is not an easy thing to do. It would require a very careful experimental technique, the use of truly monochromatic radiation and a really first-rate measurement of the line broadening as the homogenization of the compact proceeds. I believe a lot more could be done by means of X ray than was done in this particular paper.

W. ROSTOKER (author's reply)—In reply to Mr. Steinitz, the particle size distribution of the silicon powder was determined by the use of a nest of standard screens vibrated for 15 min. No agglomeration difficulties were encountered.

Of the variables which might, in addition to inhomogeneity, affect the change of magnetic properties with time, Mr. Steinitz mentions density and pore shapes. Pore shapes at high temperatures become spheroidal early in the sintering history. The amount of porosity in the repressed and unsintered condition is 4.5 pct and after sintering for 24 hr at 1400°C is only decreased to 1.9 pct. The consolidation is therefore only slight. In accordance with the demonstrated linear effect of spheroidal porosity on permeabilities there should be little effect on the homogenization experiments.

In a similar vein, Mr. Steinitz would attribute the low maximum permeabilities of the heat treated nickel-iron alloys to porosity. Again, under the conditions of treatment the rings would be expected to, and indeed do, exhibit spheroidal porosity. The author feels that the experimental work presented definitely shows such pore shapes to exercise only slight influence on permeability at 95 pct of full density. It might also be pointed out that the maximum permeabilities of 65 and 78.5 pct nickel-iron alloys in the annealed state are quite normal. As a conjecture, the cause of this trouble might rather be in small scale inhomogeneity.

The density variations were effected by submitting samples to successively higher molding pressures. The very high densities required a double pressing operation with an intermediate short time, low temperature anneal. The final sintering times and temperatures were chosen to give conveniently the range and character of porosities.

Polder and Van Santen quantitatively calculated the effect of pore character and content on dielectric properties. They suggested that the effect on magnetic permeabilities at constant field would be analogous. There is no reason to expect that the analogy should be more than qualitative. For that reason, a permeability of 100 is referred to as "low" as compared with values of several thousands at low inductions and in accordance with usual magnetics parlance.

Mr. Steinitz implies that the large differences in maximum permeability between the sintered iron of full density and porous irons are due to differences in density. The author would rather attribute this to the extremely low carbon and oxygen contents (see Table 7) and the large grain size of the high density iron due to the prolonged heat treatment in hydrogen at 1420°C. In effect, the two irons are not of comparable purity. The true permeabilities of the porous irons would best be determined by extrapolation of the straight lines of Fig 7 to 100 pct of full density.

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In reply to Mr. Glaser, the appropriate amounts of iron and silicon powders were weighed out and mixed for each ring individually. In this way, the required amount of silicon was introduced into each ring and it was not thought necessary to analyze the rings after heat treatment. There was no apparent segregation during the mixing operation or while pouring the powder mixture into the molding die. The electrical resistivities do not appear to vary from other reported values by more than about 5 pct.

The author finds himself in full agreement with the comments of Professors Rhines and Norton concerning the proper study of an inhomogeneous state by X ray diffraction methods. He also feels that the experimental and interpretive difficulties involved would necessitate a separate project. Lack of proper equipment prevented the X ray studies presented here from being more detailed. But it should be remembered that this portion of the work was intended to assist interpretation of the magnetic results. The main purpose in presenting the X ray data was to show that an apparently sharp diffraction pattern could be observed long before the structure-sensitive magnetic properties reached their ultimate values. Undoubtedly, a more careful examination of these apparently sharp lines would have indicated small scale inhomogeneity. But the pertinent conclusion to be taken was that small scale inhomogeneity affected structure-sensitive magnetic properties as severely as very small carbon and oxygen contents (T. D. Yensen, Ref. 5).

The Densification of Copper Powder Compacts in Hydrogen and in Vacuum

By C. B. JORDAN and POL DUWEZ

DISCUSSION

(*A. Squire presiding*)

A. J. SHALER*—I should like to congratulate the authors for having carried out such a precise set of experiments. It has been found useful, in sintering experimental compacts in vacuo, to make certain that the residual gas is not one which reacts with the metal. Since traces of oxygen can be kept away only with great difficulty, the technique is often adopted of using a "getter" of powder in the vicinity of the compacts, and, in addition, of permitting a small hydrogen leak to flow into the vacuum chamber. Did the authors use similar devices?

This paper brings up a question concerning the definition of the word 'sintering.' The authors restrict its use to the adhesion between particles. Kuczynski, in a paper presented at this meeting, applies the word to the growth of areas of contact between particles. I have used it to mean both these phenomena and also the dimensional changes which continue to take place after the first two have run their course. May I suggest that we should come to an agreement on the use of these words?

Fig 1 and 2 show an interesting feature: extrapolation of the curves to zero time does not give a densification parameter of zero. The higher the temperature, the higher is the intercept on that axis. These observations agree with the concept of a practically instantaneous densification taking place while the compact is being brought to heat. Such a change may be brought about by plastic deformation and primary creep. The stress pattern causing this first rapid flow is, to my mind, due to the force of attraction between the surfaces of opposite particles in the regions immediately flanking their common areas of contact. The stress is not temperature-sensitive, but at room temperature plastic deformation only proceeds until the metal in the area of contact can support it elastically. As the metal is heated, the elastic limit falls, and further plastic flow occurs. At the higher temperatures, this is followed by primary creep, and finally by the steady-state rate-reaction which the authors are seeking. If they were to recalculate their densification-parameter values, using, not the initial density of the cold compact, but the density after the compacts have been brought to temperature, the systematic deviations from linearity in Fig 3 and 4 might be eliminated. Such initial densities might be obtained by extrapolating the curves of Fig 1 and 2 to zero time.

I am naturally pleased to see that such a very well done series of experiments leads to a heat of activation (for the densification process in hydrogen) that is much higher than that for self-diffusion, in confirmation of the less elaborate results reported by Wulff and myself (*Ind. and Eng. Chem.*, (1948) **40,** 838).

J. T. KEMP*—I would like to comment on Dr. Shaler's remarks. There are apparently different interpretations of the word "sintering." It seems to me that an accurate definition of our word is essential in all metallurgy. May I point out, in this connection, that in practical metallurgy the word "sintering" has been applied to a bonding process in the preparation of ores and flue dust for furnacing. It would be unfortunate if in the area of powdered metallurgy we should establish a definition that is essentially different in meaning.

F. N. RHINES*—I think that I can answer the question by saying that I see no essential difference between the use of the term "sintering" in extractive metallurgy and in powder metallurgy; physically the same things are going on. I admit sintering is used for different end purposes in the two cases. When we resort to the sintering of lead ore mixture we are doing so to obtain a chemically reactive, loose texture of some rigidity. This is only a difference in use. After all, in powder metallurgy we sometimes deliberately produce a very porous material which has just a little strength, just as in the case of sinter cake.

P. DUWEZ (authors' reply)—We agree that it would be helpful to have well-established definitions of such terms as "sintering." Since the question has now been raised, the time might be appropriate for its consideration by some suitable committee of one or more of the metallurgical societies.

In answer to Dr. Shaler's first question, no getter nor hydrogen leak was used in our vacuum experiments, except insofar as the guard disks (used to reduce friction between specimens and trays) may have acted as getters.

Dr. Shaler's statement that extrapolation of the curves of Fig 1 and 2 does not lead to zero densification at zero time apparently overlooks the logarithmic time scale used in those figures. The intercepts he mentions are not on the line $t = 0$, but on the line $t = \frac{1}{4}$ hr. The densification parameter, as we have defined it, is necessarily equal to zero at $t = 0$, and the curves of Fig 1 and 2 would indeed intersect at $\sigma = 0$ if extended far to the left.

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Since the shortest time employed in our experiments was $\frac{1}{2}$ hr, we feel that our results should not be taken as either confirming or denying Dr. Shaler's concept of a practically instantaneous densification during the heating-up period. If the results of shorter-time experiments were such as to confirm this hypothesis, it would then be interesting to see whether the curves of Fig 3 and 4 are more nearly straight lines if the values of σ are calculated on the basis he suggests. His idea that densification is the result of several processes which successively predominate, is in agreement with the opinion we expressed in the paper at the conclusion of the section on "Interpretation of Results."

The Surface Tension of Solid Copper

By H. UDIN, A. J. SHALER and J. WULFF

DISCUSSION

(*A. Squire presiding*)

G. KUCZYNSKI* and B. H. ALEXANDER*—This paper represents a most noteworthy attempt to evaluate experimentally the surface tension of a solid metal. Because of the great importance of such measurements, any proposed method should receive the closest scrutiny before the results can be considered reliable.

In regard to the experimental method, we think that the marking of the gauge length by means of tieing knots in the wire may be the cause of some of the spread in the results. Such a knot may be expected to tighten slightly, and thus increase the gauge length, when placed under stress at high temperature. Although this effect would be very small, amounting at most to only a few times the wire diameter. A fairly tight knot in a wire will decrease the wire length by about ten times the wire diameter, thus only a slight tightening of the knot would cause considerable spread in the results.

Upon plotting the stress strain curves from the authors' data, the writers found that there was a fairly consistent tendency towards an S-shaped curve, instead of a straight line. Such an effect could be caused by the tightening of the knots.

The writers think, however, that the experimental results are fairly reliable, but that there may be other methods of interpreting them depending upon what mechanism is assumed to be responsible for the shrinkage of the wires. The authors have assumed that the stress due to surface tension results in viscous flow. It should be made clear that it has never been demonstrated that viscous flow can occur in metal crystals even at very high temperatures. The experiments of Chalmers[13] on tin, which are so frequently quoted as giving evidence of viscous flow at low stresses are by no means satisfactory. In his experiments, Chalmers found that only the initial rate of flow was approximately proportional to stress. He also found that the rate of flow varied markedly with time which, in his experiments, was less than 2 hr. Inasmuch as there is no proof of viscous flow in metals, and the authors have brought forth no conclusive evidence on this point, it may be worth while to investigate other possible mechanisms of material transport which would account for the shrinkage of the wires. The writers wish to point out that in these experiments the shrinkage of the wires can be adequately explained, according to a self diffusion mechanism. Thus, if we assume a concentration gradient for self diffusion which is a function of the radius of curvature of the wires, and assume that diffusion will occur so that the total surface area is decreased, we find the following expression for the self diffusion coefficient:

$$D = \frac{-k r_0^3 T}{\gamma \delta^3 t} \ln \epsilon \qquad [19]$$

where k = Boltzmann constant
r_0 = initial radius of the wire
T = absolute temperature
γ = surface energy
δ = interatomic spacing
t = time
ϵ = strain at zero applied stress

Eq 19 may be used to evaluate the self diffusion coefficient of copper, using the strain measurements obtained by the authors for zero stress as obtained by extrapolating their curves for 5 mil wires. By inserting a reasonable value for the surface energy (1500 ergs per cm^2) we find:

$$D = 5 \times 10^4 e^{\frac{-66,000}{RT}} \qquad [20]$$

The activation energy is of the correct order of magnitude, but the frequency coefficient is much too high, indicating that surface diffusion may be playing an important role. This discrepancy in the action constant is much smaller than the corresponding discrepancy obtained by the authors for the viscosity coefficient. The writers by no means propose that this proves that the shrinkage of the wires is due to self diffusion but we merely wish to point out that there are explanations other than that given by the authors. In this, as in any kinetic phenomena, it is necessary to study the *rate* of the process before anything can be said about the mechanism. The determination of surface tension given by the authors is based upon an interpretation of the data which embody the concept of viscous flow. The final proof of this concept will be obtained only after the time relationships confirming the authors' Eq 15 have been conclusively established. The rough linearity of the stress strain curves obtained by the authors for experiments run the same length of time should not be considered as proving that viscous flow is occurring.

H. UDIN (authors' reply)—All of the test specimens were annealed at 1000°C for an hour or more before preliminary measurements were made. During this anneal the wires recrystallize, and the greatest part of grain growth takes place. Also, the knots sinter at the cross-over points. This does not in itself eliminate the possibility of end errors, although it greatly decreases their probable magnitude. It is still possible that some extension occurs due to creep in shear at the sintered points. If so, this effect would be quite independent of and superimposed on the normal shrinkage or extension of the wire itself. Within the precision of the experimental results, straight lines satisfy the data as well as do any other simple curves. Until data of greater precision are obtained, it is futile to discuss any possible trends away from linearity.

The disagreement between Kuczynski and Alexander's Eq 19 and our Eq 18 is one of semantics and mathematics, not mechanism of flow, since Eq 18 is based on the self-diffusion concept of viscous flow. It would be interesting to learn how the mathematics leading to Eq 19 deviates from that of Eyring and of

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[13] B. Chalmers: *Jnl.* Inst. of Metals (1937) 61, 103.

Frenkel. The dependence of self-diffusion coefficient on specimen size in Eq 19 is somewhat startling.

As Dr. Orowan points out, neither the mode of flow nor its time dependence has any influence on the numerical values obtained for the surface tension of solid copper, because it is found from the interpolated value for zero strain.

A. J. SHALER (authors' reply)—Dr. Kuczynski has said, if I understand him correctly, that there may be a mechanism of material transport, no different from our atomic process, which would give him a logarithmic relationship between time and the longitudinal strain. I do not understand how he obtains an equation differing from our linear relationship. The experiments that were plotted here were carried out for various times, a random choice of times at the various temperatures. Within the limits of experimental error, these points fall on a straight line; there is no indication of a systematic deviation which would be indicative of a logarithmic relationship. I would like to ask Dr. Kuczynski if he would elaborate on why he expects this curve to be nonlinear by his method of material transport.

G. C. KUCZYNSKI—I want to say again that I do not claim that this mechanism is the true mechanism. As a matter of fact, I do not believe that it is. It is only given for the purpose of showing that something else is possible to explain the results. We have said that we are unable to distinguish which mechanism is the true mechanism because only the time relationship will give the answer to this question. The mechanism here suggested is very similar to that of closing of the cylindrical void by diffusion flow. This will take place in order to decrease the total surface area. Similarly in this case the wire by shortening its length and increasing the radius can lower the total surface. When we plot strength against stresses we may get a very similar plot to that obtained by Dr. Shaler.

L. D. JAFFE*—I first would like to congratulate the authors because this appears, if the work is correct, to be the first reliable determination of the surface energy of a solid, and I think that is going to be of tremendous importance in the years to come. I believe this paper will lay the foundation for a great deal of research both in physical metallurgy and in the more specialized field of powder metallurgy within the next few years.

I should like to raise a question with respect to one of the basic assumptions of the authors that the specimen will remain cylindrical while it is extending or contracting longitudinally. The behavior of the wires under test should be essentially analogous to the behavior of a soap film, but a soap film under the conditions used will not remain a cylinder. A cylindrical soap film, if permitted to deform under the influence of surface tension will attempt to break down. It will develop a waist whether there is an overall extension or contraction. In fact, if the length/diameter ratio is large, as it was in the wires, the soap film will tend to break up in a series of droplets. Now, should not the wires also tend to break up into droplets? If so, then the equations used by the authors may not be applicable, and the value obtained for the surface tension may not be valid.

Dr. Kuczynski pointed out that solid crystals do not ordinarily flow in a viscous fashion. That is quite true, but it has been established by recent work of Kê that grain boundaries do behave in a viscous fashion. However, if the deformation measured by the authors is primarily due to grain boundary flow, it should not be considered as uniform on an atomic scale throughout the specimen. Also from the experimental standpoint, it would appear that the stress-strain-time relationship would then depend on the grain size of the material. Grain sizes are not mentioned in the paper. If the grain sizes were determined, would the authors give the results in their reply?

Finally, is there any possibility that the difference in the behavior of 5 mm and of 3 mm wires might be associated with differences in relative grain size?

H. UDIN—We measured the wires as carefully as we could and found no variation in diameter. That was one of the reasons why we knotted it instead of using nicks or grooves in the wire as gauge points. However, after this paper was written, we began a new series of experiments in which we nicked the wire circumferentially with a 30° angle blade. Our nicks were at least a thousandth of an inch deep in a five thousandth's diameter wire, so we were actually inviting trouble if there was any tendency for the wire to pinch off, and in every case we found the opposite tendency. The wire tended to restore its cylindricity rather than to break up at the nicks.

As to the grain size and shape, I should like to point out that after the anneal the grain boundaries are found to be perpendicular to the axis of the wire except in a few cases of twins, and I cannot quite see for this type of configuration how any grain boundary flow can occur, or at least how it can affect the length of the wire.

A. J. SHALER—If this grain boundary flow were to take place it should lead to a saturation value of strain as you proceed to longer times. Just by accident I happen to have a slide in my pocket showing the stress-strain rate relationship from these experiments. I think that this answers partly Dr. Kuczynski's question and partly Dr. Jaffe's question. There is no evidence, I think, within experimental error of any saturation strain at long times (which are in this case coincident with high strain rates) either in compression or tension, nor of any departure from Newton's law of viscosity.

A. A. CENTER*—I wish to say that I am very interested in this attempt to measure the surface tension of solids. I am wondering about the analogy to soap filmed drops. They do have a tendency with increasing ratio of length to diameter of necking down and then of course of breaking up into droplets. The matter of the nicks in the copper specimens tending to heal under stress is certainly a very interesting observation and will require further study. We will hope to hear further on that. I have done some work in chemistry and physics of surfaces and think this is a very interesting attempt to measure the surface tension of solids I hope there will be further work along these lines to see if they are actually measuring either surface tension or surface energy, or something else.

J. WULFF (authors' reply)—In answer to the last comment, we have been a long time trying to find quantitative measurement for the surface tension of solids. We have been worrying in our laboratory for the last five years over how we could approach this problem and we, of course, shall repeat many of these experiments, carry them on in different atmospheres, do them with silver and gold, do them with alloys. However, we are very thankful that we were able to get this far in five years.

E. OROWAN†—I should like to discuss some remarks made during the discussion, rather than the paper itself; first, however, I would say how much I enjoyed the report on this very ingenious piece of work.

The final result does not depend on the exact nature of the law of viscous flow; in principle, the method consists of observing that particular value of the applied force at which no flow occurs.

Viscous flow in a polycrystalline metal may be either sliding of the grains upon their neighbors, or crystallographic slip ("recovery flow," due to the continued removal of strain hardening by thermal agitation). Grain boundary sliding in general slows down with time, because the unevenness of the grain boundaries resists the continuation of the sliding movement; in the present case, however, the boundaries were nearly plane. On the other hand, they were also nearly perpendicular to the axis of tension, so that boundary sliding may not have played an important part; the main part of the deformation was probably by intracrystalline slip.

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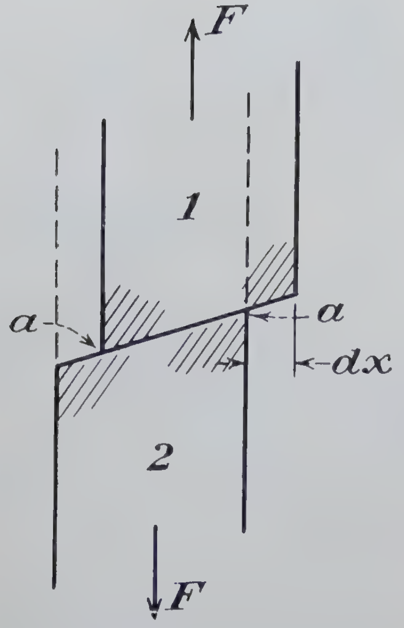

FIG 7—Energy involved in slip.

One can prove that the tendency to necking, which is typical of plastic deformation governed by a stress-strain curve of the usual type, is practically absent if the deformation obeys Newton's law of viscosity. Yet it is difficult to see why cylindrical single crystals should always retain a circular cross-section during flow. If they flatten, the value of the surface energy derived from the measurement will be different from that obtained with the assumption of a circular cross-section, although the difference will amount only to a factor of order unity.

What the authors have carried out is the counterpart of the well-known soap film experiment of Dupré. Let the forces F produce slip in a crystal with the operative slip plane indicated by the dotted line in Fig 7. If the resistance to slip is of a purely viscous nature, it vanishes for infinitesimally slow deformation, and then the forces F are opposed only by surface forces. Let ω be the (free) surface energy per unit of area of the slip plane. If the displacement between the parts 1 and 2 of the crystal increases by dx, new surfaces of area bdx are laid open at the re-entrant corners a, where b is the width of the slip plane perpendicular to the plane of the figure. The increase of the total surface energy is $2\omega b\ dx$, and this must be equal to the work done, $F\ dx$; hence,

$$\omega = \frac{F}{2b}.$$

This is identical with the relationship between equilibrium force and surface energy in Dupré's soap film experiment.

Clearly, the surface force that resists the applied forces F in Fig 7 must be the attraction of the opposite quadrants (shaded in the figure) resolved in the slip direction. In fact, it can be proved generally that the resolved attraction of two opposite space quadrants, per unit length of the edge, is equal to the specific surface energy of their boundary planes. This theorem, however, is valid only if the material is a continuum in the sense of the classical theory of capillarity, or at least behaves like a continuum (homopolar materials may do so; to ionic crystals, the theorem cannot be applied).

A. J. SHALER—I think I speak for the other authors as well as for myself in thanking Dr. Orowan for his great interest in this work and for clearing up several points so much more beautifully than I could have done it.

Concerning the question of the cylindricity I should like to bring up once again that in the measurement of the surface tension the change from a circular cross-section to an elliptical one does not matter because at the point of measurement where zero strain occurs there is also no deformation in the cross-section. Therefore, the question of the strain pattern does not influence the measurement of the surface tension (or surface energy). If the process of flow is by slip there should be a barrier stress which would give us, in the curve of strain or strain rate against stress, a discontinuity on the zero-strain axis. It is very possible that this process is the actual one operating, and that our experimental measurement cannot detect the flat portion in the curve.

We have discussed the matter of calling our value surface tension or surface energy, and we have come to the conclusion that we ought to call it surface tension, for the reason that this measurement is a mechanical one. We are dealing with a force and surface tension is a force. An energy would only be exhibited at other than zero strain. We may be wrong. We intend to make surface tension measurements on metal single crystals and on silver chloride; we may be able then to untangle some of these problems by comparing the results between ionic crystals and metal crystals.

Self-diffusion in Sintering of Metallic Particles

By G. C. KUCZYNSKI

DISCUSSION

(*F. N. Rhines presiding*)

A. J. SHALER* and H. UDIN*—Bonding, and the increase in contact area, form two of the series of phenomena collectively known as 'sintering.' A third one of these is involved in changes in dimensions of the whole compact. Dr. Kuczynski's Fig 1, in which the center of the sphere does not approach the surface of the plate, shows that he is not concerned with the last of these phenomena. On the other hand, Frenkel's work is exclusively concerned with changes in dimensions. Dr. Kuczynski's rather unfortunate remarks about Frenkel's work are therefore beside the point. The work of Wulff and myself, quoted by the author, has also been primarily concerned with what we call the 'second stage of sintering,' in which such systems as may be represented by Kuczynski's model of a sphere and a block are no longer in existence. The work of Pines also falls in this category.

Neither does Dr. Kuczynski's very masterful experimental work represent a solution to the problem of bonding. It does not seek to answer the question of why particles approach one another and form a weld in the first place. Such a study clearly reveals that the area of contact is initially rapidly deformed by direct mechanical flow caused by the same force of attraction. This initial deformation is neglected here.

On the other hand, students of the phenomena of sintering must not underestimate the very important contribution that Dr. Kuczynski does make in this paper. It is a well-worked out study of the mechanism of 'spheroidization' of the voids, the first manifestation of which, during sintering, is the growth of the areas of contact, with no change in the dimensions of the compact. This study is very valuable as a basis for predicting the development of the strength of such compacts as filters and certain porous bearings, in which the second stage of sintering is never reached.

A few more specific points may be brought up here. If, in Table 4, the data are extrapolated to zero time, it is easily seen that x is still considerable. I believe that this initial very rapid increase in x is due to plastic flow. If the author had used values of x/a based, not on $x = 0$ at $t = 0$, but on some value, based on later measurements, of $x = x_0$ at $t = 0$, his power relations would have been lowered. Thus, whereas he demonstrates that surface diffusion and what he calls volume diffusion are the mechanisms of spheroidization because the radius of curvature at the contact area shows a 5th or 7th power time-dependence, it is possible that, by taking into account the initial rapid plastic flow, the power relation may be considerably altered. Has Dr. Kuczynski made any calculations taking this into account? It is possible that such a treatment of the data would modify the tendency towards higher-powered relationships with finer particles.

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Dr. Kuczynski has sought to demonstrate that with large particles the mechanism of vacancy diffusion is predominant in the growth of the areas of contact. Frenkel's viscous-flow theory also requires that the units of flow are diffusing vacancies. Yet Kuczynski categorically states that the viscous-flow theory is not valid. I wonder if he could clarify his position in this matter. Dr. Kuczynski states that if Frenkel's viscous-flow mechanism is responsible for sintering, the relationship between the radius of the area of contact and the time of heating should be a quadratic function. Although there is an error in the numerical constant in Eq 2, taken from Frenkel, this statement is true. Experiments which are based on this relation were published last year by Wulff and myself. They show a heat of activation for the flow process (in a hydrogen atmosphere) considerably higher than that for self-diffusion, found by the author. This (I quote the author) "by no means adequate test of theory" is strongly supported by the results of the much more adequate results found by Jordan and Duwez, which were reported at this meeting, and in which the heat of activation in hydrogen is found to be 80,000 cal per mol. These figures appear to indicate that the flow mechanism in the second stage of sintering is essentially different from the spheroidization process which Kuczynski has studied here, and for which he arrives at a heat of activation of 56,000 cal per mol for copper. I believe that our experiments, and those of Jordan and Duwez, indicate the existence, in the earliest stage of sintering, of a rapid flow rate, such as in conventional primary creep, followed by a viscous flow. These mechanisms are responsible for the densification or swelling of compacts. Superimposed on these, the spheroidization of voids proceeds by the two mechanisms adduced by Kuczynski. This spheroidization contributes to the increase in strength of the compact but cannot explain changes in density. That these two processes are going on at the same time is shown by Kuczynski's Fig 2. His calculations are based on the relation between the radius of curvature at the edge of the contact area and the x/a ratio. Fig 2*a* shows a large radius of curvature and a small x/a ratio. Fig 2*d* shows, at a higher temperature, a much smaller radius and a larger ratio. These results are in direct conflict unless two mechanisms are at work, having different heats of activation. One is predominant at low temperature (the spheroidization), the other at high temperature (the viscous flow preceded by primary creep and perhaps by appreciable instantaneous plastic flow, in fine particles). Spheroidization produced no densification; that is, the sphere center does not approach the block in Fig 2*a*. Plastic or viscous flow does cause densification, and the center approaches the block, as in Fig 2*d*. It is not fair to base such a conclusion on two pictures which Kuczynski states to be unreliable because of lack of sphericity. But further evidence that one single mechanism may not be capable of explaining his results may be found in Fig 5, which presumably refers to copper and not to silver (the caption on Fig 4 being here applicable). In this figure the points referring to the 700° experiment at 4, 8, and 41 hr have not been plotted in accordance with the data in Tables 1 and 3. If the tables are correct, the points for 8 and 41 hr should be plotted much higher, and the average of the 5 points for 4 hr should also be higher. The line through these corrected points has a much greater slope than those shown, so that the dominant mechanism at low temperatures is not the same as at high temperatures. Plotting the widely scattering points found at 600° gives, at least initially, an even greater slope.

G. C. KUCZYNSKI (author's reply)—J. Frenkel in his paper entitled "Viscous Flow of Crystalline Bodies under the Action of Surface Tension" published in *Jnl. of Physics* (U.S.S.R.) (1945) **IX**, 385–391 does discuss the problem of bonding or as he calls it "welding" of the crystalline spherical particles without appreciable change of dimensions. He also states in this paper that the units of viscous flow are diffusing vacancies. The flow takes place by atoms moving to these vacancies preferably in the direction of the applied force. There is however another diffusion flow which does not require this acting force. If there is a gradient of vacancy concentration in a region of the body the atoms will move into this region. This type of mechanism was assumed in my paper. Obviously the kinetics of these two mechanisms and resulting time relationships are different. Viscous flow can produce sintering in the case of glass where the relationship $x^2 \sim t$ predicted by Frenkel was indeed observed. In the analysis of any kinetic problem the time relationship is typical and far more important than the temperature dependence. The latter one may often be misleading.

As to the specific points stressed by Dr. Shaler I have to admit that Tables 1 and 2 contain three errors, all typographical. Some of them can easily be corrected by comparison with Table 3. In one case the diameter of the interface was introduced instead of its radius.

I have replotted the results from Table 1 and 2 on nonlogarithmic scale $\left[\left(\frac{x}{a}\right)^5 / t\right]$ and obtained straight lines which all pass through the origin, except for the curve for copper heated at 700°C. The deviations at 700°C occur for small periods of time when the diameters of the interfaces are small (few microns). Under such conditions the possible error is larger than in other cases. It is therefore quite possible that these deviations are not real.

Although the method described in the paper under discussion is not too accurate it most certainly is able to distinguish between two consecutive powers of the interface diameter.

M. BEVER*—The experimental methods described in this paper are of real interest. From the standpoint of techniques, any new quantitative use of metallographic observations is an interesting and welcome development.

A question should be raised concerning the choice of atmospheres in the sintering experiments. Hydrogen is soluble in solid copper and silver and oxygen is soluble in silver. Even if these gases are considered to have only negligible effects in solution, hydrogen can reduce oxides that may be present on the surface. It is well-known that such reduction leads to surface layers of very great activity. It is desirable to exclude even the possibility of such active surface layers from experiments in which surface phenomena may play a part.

G. C. KUCZYNSKI—I was aware of this difficulty. However I have run some silver samples in hydrogen and oxygen at 700 and 800°C for the same periods of time and no difference was observed; and recently a few copper specimens were run in an argon atmosphere at 900 and 1000°C. There was not any appreciable difference between these and those heated in hydrogen. Tentatively therefore I can state that in the case of these two metals any nonoxidizing atmosphere does not seem to have an appreciable influence upon the bonding of particles.

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Evaluation of pH Measurements with Regard to the Basicity of Metallurgical Slag

CHARLES W. SHERMAN* and N. J. GRANT,* Junior Member AIME

The correlation of the high temperature chemical properties of slag-metal systems with some easily measured property of either slag or metal at room temperature has been the goal of both process metallurgists and melting operators for many years.

There are several rapid methods for estimating various constituents in steel in addition to the conventional chemical methods which are quite fast, but these do not reveal the nature of the slag as a refining agent, which is of primary interest to the steelmaker.

Furthermore, there are several methods for examining slag, the three principal ones being slag pancake, petrographic examination, and the previously mentioned chemical analysis. The main objection to the last two is the time required to make a satisfactory estimate of the mineralogical or chemical components. The objection to the first is the inadequacy of the information obtained.

A new technique has been developed by Philbrook, Jolly and Henry[1] whereby the properties of slags are evaluated from an aqueous solution leached from a finely divided sample of slag. It is known that the pH or hydrogen ion concentration (of saturated solutions that have dissolved certain basic oxides, notably calcium oxide) will indicate a pronounced basicity.

Philbrook, Jolly and Henry devised the pH measurement technique in order to supply open hearth operators with a fast, reasonably accurate method of estimating slag basicity. They offered the method as an empirical observation and made no claims as to its theoretical justification. The results were presented as an experimetally observed relationship which applied over an important range of basic open hearth slags. They found that, in plotting the measured pH against the basicity, the best relationship existed between the pH and the log of the simple V ratio, CaO/SiO_2.

Extensive investigation also showed that there were several variables in the experimental technique that influenced the results and necessitated following a standard procedure to obtain reproducible pH readings. These variables were: 1. Particle size of the slag powder used. 2. Weight of sample used per given volume of water. 3. Time of shaking and standing allowed before the pH was measured. 4. Exclusion of free access of atmospheric carbon dioxide to the suspension. 5. Temperature of the extract at the time the pH was measured.

In subsequent investigations of the pH method by Tenenbaum and Brown[2] and by Smith, Monaghan and Hay[3] the general conclusions of Philbrook's work were reaffirmed. It was the object of the present investigation to extend the technique to a point where it could be used to evaluate slags of all types.

Experimental Results

PARTICLE SIZE OF SLAG POWDER

A large sample of commercial blast furnace slag of intermediate basicity (V-ratio 1.15) was selected for the study. The slag had been put through a jaw crusher until all of it passed through a 20 mesh screen. Five fractions of this crushed material were separated, −20 to +40, −40 to +60, −60 to +100, −100 to +200, and −200 mesh.

A representative sample of 0.5 g was removed from each fraction and the pH determined using the method of Philbrook. Check pH analyses on the sample fractions varied due to the different amounts of shaking. To eliminate this variable, a mechanical shaker was employed. In order to know the exact time of contact between the slag and water, it was found necessary to filter the extract at the end of the shaking period. Using the mechanical shaker and a filtering apparatus, similar runs were made on the five fractions for contact times of 5, 10, 20, and 40 min. Random checks gave reproducible results within 0.02 pH. The data are plotted in Fig 1.

It can be seen from the plot that each slag fraction is hydrolyzed to an extent that is roughly proportional to the surface area exposed to the water. The (−100 to +200) mesh material changed very little in pH after 10 min. shaking time. The curves are symmetrical and lie in proper relation to one another. The −200 mesh curve appears to be somewhat flatter than the others, but this can be attributed to the portion of very fine material that is not present in the other fractions.

The closeness of the (−100 to +200) mesh curve to the −200 mesh curve and the fact that a −100 mesh sample would contain amounts of slag down to 1 or 2 microns in diam were considered sufficient reasons for selecting a −100 mesh sample as representative of the whole sample of slag for the purposes of this investigation.

New York Meeting, February 1950.
TP 2715 C. Discussion of this paper (2 copies) may be sent to *Transactions* AIME before April 1, 1950. Discussion is tentatively scheduled for publication in November 1950. Manuscript received June 17, 1949.

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* Research Assistant in Metallurgy and Associate Professor of Metallurgy, respectively, Massachusetts Institute of Technology, Cambridge, Mass.

[1] References are at the end of the paper.

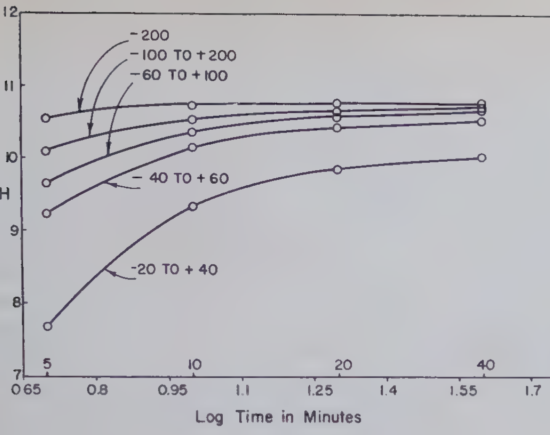

FIG 1—Effect of shaking time on pH for various particle sizes.

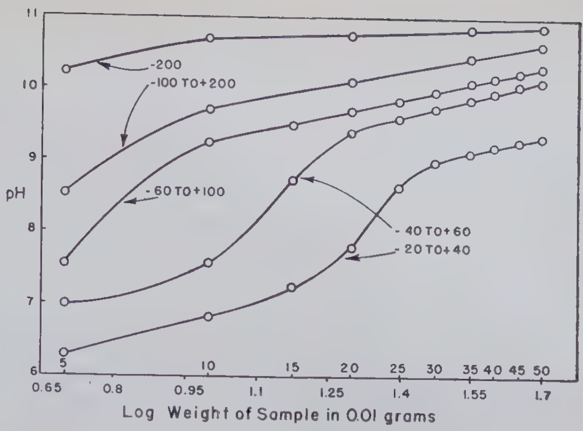

FIG 2—Effect of weight of sample on pH for various particle sizes.

EFFECT OF WEIGHT OF SAMPLE ON pH

The same commercial blast furnace slag that had been used in the study of particle size was also employed in determining the effect of weight of sample on pH. Portions of the five screen sizes were removed and weighed carefully on an analytical balance. The smallest sample taken was 50 mg and the largest sample was 500 mg. (The procedure for weighing, shaking, and filtering remained unchanged, and the time of contact between the water and the slag was held constant at 10 min.) The data are plotted in Fig 2.

It can readily be seen from the plot that the curves assume the general characteristics of potentiometric titration curves for acid-base reactions. This type of curve has a straight line portion on either side of the neutralization point. It was considered important that the sample size selected as a basis for a standard should be well within the straight line portion of the curve in order to compare different slags satisfactorily. As a consequence, the weight of sample selected as standard for the rest of the investigation was 0.5 g.

In order to shift the neutralization point further to the left, it was decided that the distilled water should be boiled to reduce the amount of acid-forming CO_2.

Any pH value on a slag extract of less than pH 9 should be considered of doubtful value since it occurs in a region where the curve bends toward the neutralization point.

STANDARD TECHNIQUE USED FOR pH MEASUREMENT

Weigh out a representative 0.5 g sample of slag which has been powdered so that the entire sample will pass through a 100 mesh screen. The sample should be dry and free of contamination. Weighing of each sample is recommended in order to obtain reproducible results; however, an ordinary trip balance may be used satisfactorily.

Place the sample in a clean, dry 250 ml Erlenmeyer flask. Measure with a pipette 100 ml of previously boiled, distilled water and add to the sample in the flask. As the water contacts the slag, note the time of contact. After the pipette drains, stopper the flask tightly and place in a mechanical shaker. This type of agitation prevents caking and agglomeration of the sample on the bottom of the flask.

Remove the flask from the shaker at the end of approximately 9½ min. and pour the suspension onto a glass frit filter as the timer reaches 10 min. This sets the exact time for contact between the water and the undissolved residue remaining.

The solution should be filtered under suction in order to complete the operation as rapidly as possible. The solution is caught in a test tube suspended inside an ordinary vacuum flask. Remove the test tube and stopper it tightly. Shake well to mix the solution thoroughly. Place a 3–5 ml sample in the test cup of a precision pH meter and measure the pH of the solution with the previously calibrated meter.

The time consumed for determining the pH on each sample by this method was about 15 min. This is exclusive of the time necessary for preparation of the slag powder and the time for weighing. It was found that results could be duplicated to ±0.03 pH as long as careful attention was paid to the various steps in the standard technique.

CORRELATION OF pH OF BLAST FURNACE TYPE SLAGS WITH COMPOSITION

Using the standard technique, as described in the previous section, a set of slags submitted in connection with the Doctor's thesis of Gerald G. Hatch was checked.

The analyses of these slags are reported in the paper of Hatch and Chipman[4] and will not be repeated here. In general, the slag compositions covered a much wider range of values for the four main constituents than is found in the typical commercial blast furnace bisilicate slags, but they are free of MnO. These limits of composition variation are as follows:

	Pct
CaO	16–52
MgO	0–38
SiO_2	14–53
Al_2O_3	0–39
S	0–4.5

Fig 3 contains a plot of the pH of each slag against its molar lime-silica ratio. In a similar manner Fig 4 relates the pH to the general molar basicity ratio, $\frac{CaO + MgO}{SiO_2 + Al_2O_3}$. These two plots are included to illustrate the diversity of the slag compositions in comparison with the slags used by Philbrook, Jolly and Henry. These authors were able to correlate their values with a plot similar to Fig 3, as were Smith, Monaghan and Hay.[3] In neither instance do Fig 3 and 4 show a relationship between the chosen basicity value and the measured pH.

In Fig 5, a plot of EXCESS BASE against pH was tried. The quantity, EXCESS BASE, in this case is similar but not the same as the quantity first

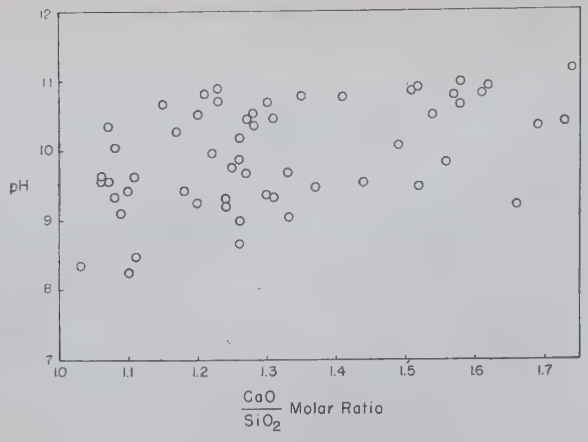

FIG 3—Effect of simple V ratio on pH for blast furnace type slags.

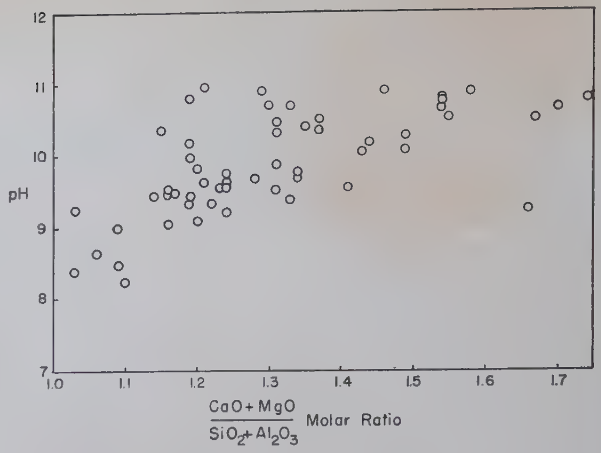

FIG 4—Effect of $\frac{CaO + MgO}{SiO_2 + Al_2O_3}$ on pH for blast furnace type slags.

calculated by Grant and Chipman.[5] In this instance, a neutral slag is assumed to be of the bisilicate type, that is, $MgO \cdot SiO_2$, and $CaO \cdot SiO_2$. Grant and Chipman had selected a monosilicate slag as a neutral slag in their treatment of open hearth slag. Otherwise, the term EXCESS BASE is computed in the same manner for the study of blast furnace type slags. The main reason for selecting a bisilicate slag as a neutral slag is that it is known that monocalcium silicate is more stable with respect to water than is dicalcium or tricalcium silicate. This treatment of solid slags in no way contradicts the assumption that Grant and Chipman used to explain the behavior of liquid open hearth slags.

It should be pointed out that Fig 5 is the plot of millimols of EXCESS BASE per 0.5 g sample against pH. One of the practical limitations of this type of basicity measurement is the variation in the number of millimols of slag in 0.5 g. The replacement of CaO by large amounts of the lighter molecule of MgO will make the number increase, whereas the replacement of SiO_2 by substantial amounts of Al_2O_3 will cause it to decrease.

The aqueous solubilities of the various oxides found in slags formed the basis of the basicity value used in plotting Fig 6. It was noted that $Mg(OH)_2$ had the largest of the solubility products after $Ca(OH)_2$, but even its value was not of sufficient order of magnitude to seriously interfere as long as there was a reasonable amount of CaO present. The pH of a pure aqueous solution saturated with $Mg(OH)_2$ can be computed and is found to be between pH 10 and pH 11, depending on the data used. The presence of $Ca(OH)_2$ greatly suppresses the hydrolysis of MgO. Since the extracts are not at equilibrium and are not saturated, it can be assumed that the MgO does not have an influence on pH's over 9.

The relationship between millimols EXCESS CaO and pH in Fig 6 seems quite good when it is realized that many of these slags are not fully matured and do not represent final equilibrium slags.

The calculation of EXCESS CaO involves the same procedure as the calculation of EXCESS BASE. After the value for EXCESS BASE has been found, it is multiplied by the CaO fraction of the total bases present in the slag. For example, if the slag contains 80 pct (molar) CaO and 20 pct (molar) MgO of the bases present, then the EXCESS CaO will be four-fifths of the calculated EXCESS BASE.

It should be repeated that the pH values found here are not equilibrium values but can be applied to a particular set of conditions. Qualitatively, it can be stated that longer shaking times would decrease the slope of the line shown in the various figures while shorter times would increase the slope.

CORRELATION OF pH OF OPEN HEARTH TYPE SLAGS WITH COMPOSITION

The same investigation that was carried out on blast furnace type slags was repeated for a set of open hearth type slags that had been used in the study of sulphur equilibria by Grant and Chipman.[5]

The composition range found in these slags is far larger than would be found in the ordinary commercial open hearth slags. The most complex slags contain varying amounts of nine different constituents.

In the calculation of EXCESS BASE for this investigation, the assumption was made again that a bisilicate slag is a neutral slag. The compounds SiO_2, Al_2O_3, and Fe_2O_3 were considered acidic and equivalent to each other on a molar basis. Also, the compounds CaO, MgO, FeO, MnO, CaS, and CaF_2 were considered basic and equivalent to each other on a molar basis. In order to compute the EXCESS BASE for a given weight of slag, subtract the acids from the bases and the remaining is the value for EXCESS BASE.

The calculation of EXCESS CaO is made by multiplying the EXCESS BASE by the CaO fraction of the total bases present in the slag. The compounds CaS and CaF_2 are included with CaO in computing the EXCESS CaO.

A plot of EXCESS BASE against pH is shown in Fig 7. The scatter of points is similar in appearance to that found for blast furnace type slags. There are more slags with higher pH's. A large portion of the open hearth type slags have pH values between 11 and 12 while the more neutral blast furnace slags seldom exceed a pH of 11. There is no significant correlation between EXCESS BASE and pH.

In Fig 8, EXCESS CaO is plotted against pH and the resulting straight line relationship is found to be quite similar to Fig 6, except that the points occur in the upper portion of the graph.

Fig 9 is a combination of Fig 6 and Fig 8 plotted together. The straight line relationship found in each case separately is the same for both types of slag. A close inspection of the plot will show that there are blast furnace slags that extend up into the more basic region of the open hearth slags, and,

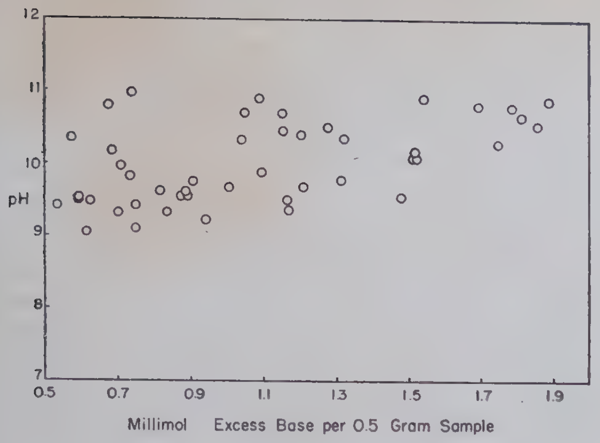

FIG 5—Effect of excess base on pH for blast furnace type slags.

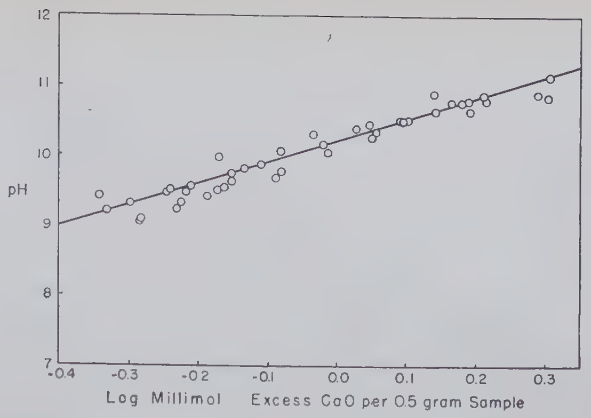

FIG 6—Effect of excess CaO on pH for blast furnace type slags.

conversely, some of the more neutral open hearth slags are found in the region of blast furnace slags.

Discussion of Results

THE pH METHOD OF ESTIMATING SLAG BASICITY

As mentioned previously, the most serious limitation in the use of the pH method as a research tool would be the variation in the number of millimols of slag in a definite weight of sample when composition varies over a wide range of molecular species of widely different molecular weights. In other words, a chemical analysis would still be necessary to check the pH results if it were expected that significant variations might occur in the low molecular weight (MgO) or high molecular weight (Al_2O_3) oxides from heat to heat.

One of the criticisms leveled against the pH method is its inability to predict V-ratios closely. This is not the fault of the pH method, but perhaps is due to the inadequacy of the V-ratio. All previous investigators of the pH method[1,2,3] have reported some sort of correlation between the pH of the slag extracts and the V-ratio in either its ordinary or modified form. However, Smith, Monaghan and Hay[3] in discussing the results of their conductance measurements infer that CaO is the controlling constituent responsible for the conductance effect. They state that it appears that the extent to which the CaO is leached out of compounds and solid solutions in the slag is in some way proportional to the V-ratio.

Since it has been found that the pH method gives a satisfactory value of EXCESS CaO, it would be expected that EXCESS CaO and the V-ratio would not correspond in all cases. This is what was found by Philbrook. The pH method proved satisfactory for his V-ratios of 2.5 to 4.

The institution of the pH method for estimating EXCESS CaO could be accomplished with several modifications in the technique reported in this investigation.

The accurate weighing of samples would not be necessary, but since the determination would be performed by laboratory personnel, the sample could be weighed in the same manner as for the iron oxide determination which commonly uses a 0.5 g sample.

Mechanical agitation of the sample is to be preferred to intermittent shaking because it prevents caking and agglomeration of the sample on the bottom of the flask.

Boiled distilled water is a safeguard against too much CO_2 in contact with the sample. A mechanical shaker and boiled distilled water usually are employed in the steel works laboratory for the determination of phosphorus. Their use would entail the purchase of no new equipment or reagents.

The filtration of the solution after a definite time of contact between the sample and the water could probably be eliminated. This step was used to determine the exact effect of time of contact on the resulting pH. However, the desirability of a set procedure should be emphasized.

The determination of the pH of the aqueous suspensions should be performed in a section of the laboratory where there is a minimum amount of acid fume. Free H_2S, HCl, NO_2 and other acidic gases have a very deleterious effect on the pH's of the basic solutions.

ANALYSIS OF BLAST FURNACE SLAG-METAL DATA IN TERMS OF EXCESS CaO

The quantity EXCESS CaO as measured by the pH method is limited in its general usefulness unless combined with additional information to determine the EXCESS BASE value for the slag. In certain instances, this might be practical to do. Whenever other oxides such as MnO or MgO remain low or are absent altogether, the EXCESS CaO value might be combined with the chemically determined FeO content to give a reasonable estimate of overall basicity.

When the basicity of the slag has been estimated in this way, any properties that vary directly with basicity can be determined. One of the prime interests of the steelmaker is sulphur control. It is known that sulphur distribution depends on basicity of the slag. With these considerations in mind, it might be expected that the use of pH values alone to determine limiting sulphur ratios would be restricted to the case where there is no FeO present, such as the typical blast furnace slag. The slags of Hatch and Chipman[4] used in this study were free of MnO and FeO, but contained more than residual amounts of MgO. Comparing their slags in two different ways, they found that it was necessary to make some modification in the desulphurizing effect of MgO. Both the $\frac{CaO + MgO}{Al_2O_3 + SiO_2}$ ratio and the EXCESS BASE per 100 g values showed a rather wide scatter of points when plotted against the sulphur ratio.

Realizing that Hatch and Chipman, in formulating their value for EXCESS BASE, had made many of the same assumptions that were used in this

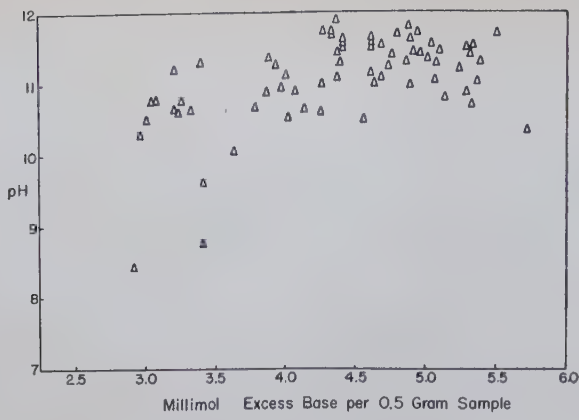

FIG 7—Effect of excess base on pH for open hearth type slags.

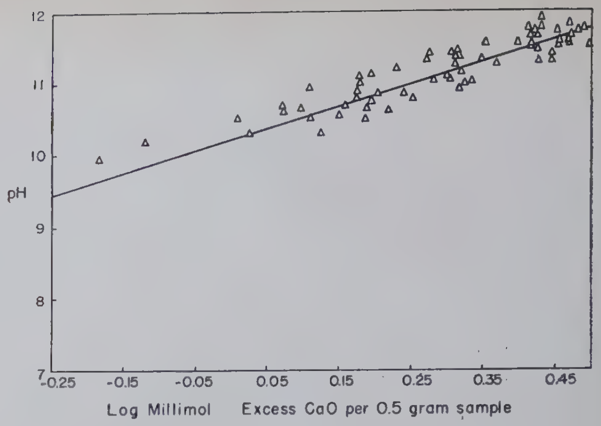

FIG 8—Effect of excess CaO on pH for open hearth type slags.

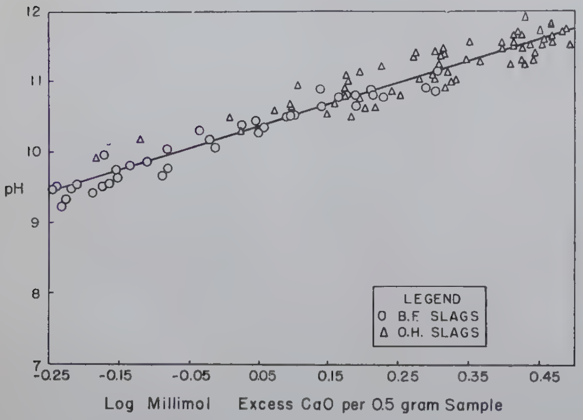

FIG 9—Effect of excess CaO on pH for blast furnace and open hearth type slags.

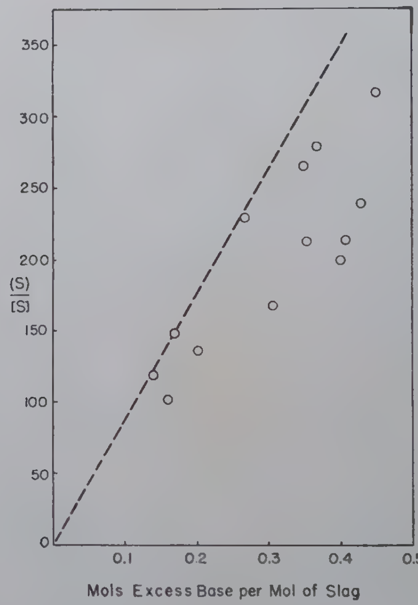

FIG 10—Effect of excess base per mol of slag on sulphur ratio for heats of Hatch and Chipman made at 1500°C.

investigation, it was thought that a better comparison might be obtained if the slags were referred to one mol of slag instead of 100 g, since there was a significant variation in the amounts of low molecular weight (MgO) and high molecular weight (Al_2O) oxides present. For the calculation of one mol of slag, it was assumed that the neutralized bases, CaO, SiO_2, MgO, Al_2O_3, and others, were one molecular species, and the "free" or EXCESS BASE was a separate molecular species.

Fig 10 shows the effect of EXCESS BASE per mol of slag on the sulphur ratio where the CaS is considered to be a base along with CaO and MgO. The point on the line drawn represents heat H-24 which has essentially no MgO. The two points that are very close to the line represent heats H-28 and H-51 which have approximately 1.5 pct MgO in the slag. Points progressively further off the dotted line show increasing MgO content.

Fig 11 is a plot of EXCESS CaO per mol of slag against the sulphur ratio. The CaS present is considered as a part of the CaO. The relationship in Fig 11 is very good, passing through the origin and showing very little deviation from a straight line relationship.

In this particular instance (MnO free slags), the pH value will give a satisfactory estimate of the basicity of blast furnace slags. Fig 12 shows the relationship between pH and the sulphur ratio for these slags. The log of the sulphur ratio must be plotted against pH since pH is a log relationship. The scatter of points is due to the variation of the number of millimols of slag in 0.5 g sample.

A similar plot of EXCESS CaO against the sulphur ratio for the open hearth slags was attempted, but the relationship was extremely poor, emphasizing the necessity for additional information to obtain the value for EXCESS BASE which has been correlated previously with desulphurization.[5]

Conclusions

1. The pH of the slag extracts has been studied over a very wide range of slag compositions varying from neutral bisilicate slags of the blast furnace type to the highly basic slags achieved in the open hearth process.

2. It has been found that the pH of an aqueous solution extracted from powdered slags, using a standard tech-

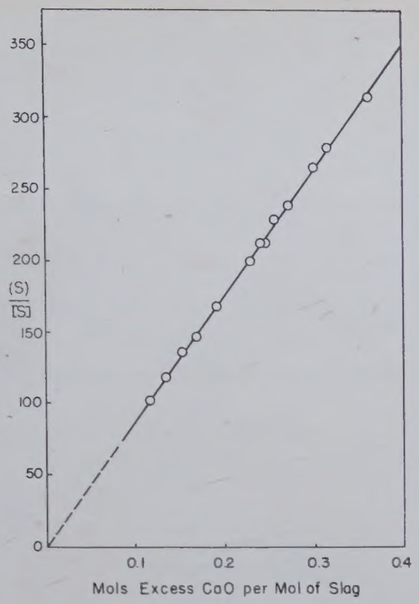

FIG 11—Effect of excess CaO per mol of slag on sulphur ratio for heats of Hatch and Chipman made at 1500°C.

nique, varies directly with the number of mols of EXCESS CaO present in the sample. EXCESS CaO is defined, in a manner similar to EXCESS BASE, as the amount of CaO remaining after subtracting the total mols of ACIDS from the total mols of BASES. The CaO is considered to be present in the EXCESS BASE in the ratio: $\frac{\text{TOTAL MOLS CaO}}{\text{TOTAL MOLS BASES}}$. The expression, EXCESS BASE, was determined on the basis of the following set of rules.

a. One mol of base neutralized one mol of acid.

b. The compounds CaO, MgO, FeO, CaS, and CaF_2 were considered basic and equivalent to each other on a molar basis.

c. The compounds SiO_2, Al_2O_3, and Fe_2O_3 were considered acid and equivalent to each other on a molar basis.

3. In addition, it has been found that the quantity, EXCESS CaO, is useful in estimating the desulphurizing power of certain MnO-free blast furnace slags for it is shown that the sulphur ratio in these slag-metal systems is controlled by the EXCESS CaO per mol of slag. For the calculation of one mol of slag, these additional rules were followed:

d. The neutralized acids were considered one molecular species.

e. The EXCESS BASES were considered a separate molecular species.

4. For MnO-free blast furnace slags, the pH of the slag shows a close relationship to the desulphurizing ratio; however, the pH is not closely related to the desulphurizing ratio of the basic open hearth.

Acknowledgments

The authors wish to thank the American Iron and Steel Institute that is sponsoring a steelmaking research program at the Massachusetts Institute of Technology, for its support of the above work.

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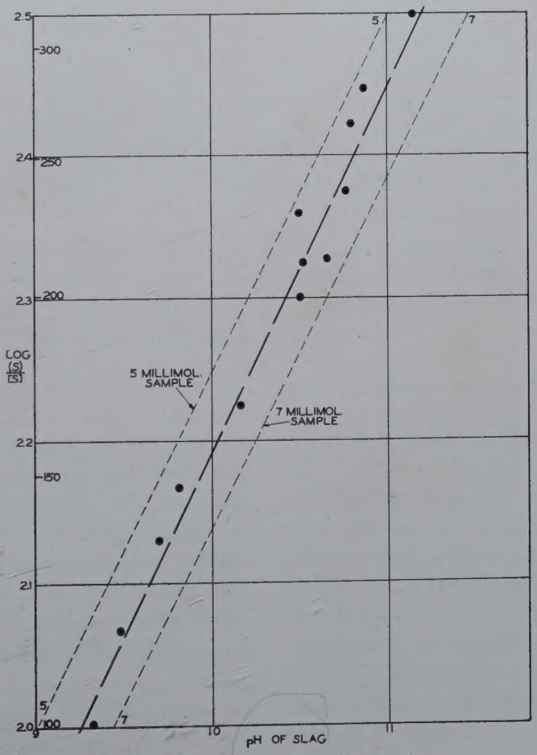

FIG 12—Effect of pH on sulphur ratio for heats of Hatch and Chipman made at 1500°C.

The Relation Between Indentation Hardness and Strain for Metals

J. H. PALM*

Experiments have shown[1,2] that the formula

$$S = S_t - (S_t - S_e')e^{\frac{-\eta}{\eta_c}} \qquad [1]$$

expresses very well the relation between the true stress S and the true strain η, $\left(\eta = \ln\frac{l}{l_0} = 2\ln\frac{d_0}{d}\right)$, for uniform monotonic deformation of plastic metals in single tension and compression (Fig 1). S_t (*asymptotic* or *final* stress), S_e' (*threshold* stress) and η_c (*characteristic* or *specific* strain) are constants, the significance of which immediately follows from Fig 1. Only at the initial stages of deformation the experimental curve runs below the theoretical curve. This may be due, at least partly, to the uneven stress distribution caused by the anisotropy of the crystals. It is now obvious that a similar formula

$$H = H_t - (H_t - H_e)e^{\frac{-\eta}{\eta_c'}} \qquad [2]$$

might be valid for the relation between the hardness and the strain. The hardness can be only a function of the strain and must therefore be independent on the hydrostatic tension present in the neck during straining. Hence, if Eq 2 is correct it will also represent the relation between hardness and strain in the middle section of the neck, the strain of which is generally assumed to be almost or fully homogeneous. For aluminum, copper, and several copper alloys it is indeed observed that Eq 2 agrees very well with the experimental Vickers hardness-strain relation from zero strain on up to the strain at fracture. Moreover η_c' is, for several metals fairly equal to η_c. Hence

$$H = C_1 + C_2S \qquad [3]$$

C_1 and C_2 are constants during uniform uniaxial tension. Eq 3 was also obtained for copper by Voce.[3] According to Hencky's theory[4] the ratio of the Brinell or Vickers hardness and the yieldstress (expressed in kg per mm²) of a non-strainhardening metal is approximately equal to 2.8. If Eq 1, 2 and 3 are correct the ratio H_t/S_t must accordingly be the same for all plastic metals and be equal to 2.8. It is now experimentally established that this ratio varies between 2.7 and 3.1 with a mean value of 2.9. Taking into account that H_t and especially S_t can be obtained only by extrapolation from the range of rather low strains, the agreement with the theory is very satisfactory.

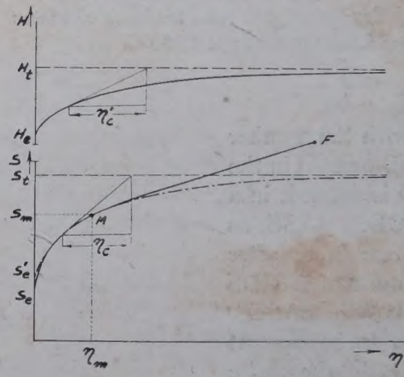

FIG 1—Schematic true stress-true strain and Vickers hardness-true strain relation.

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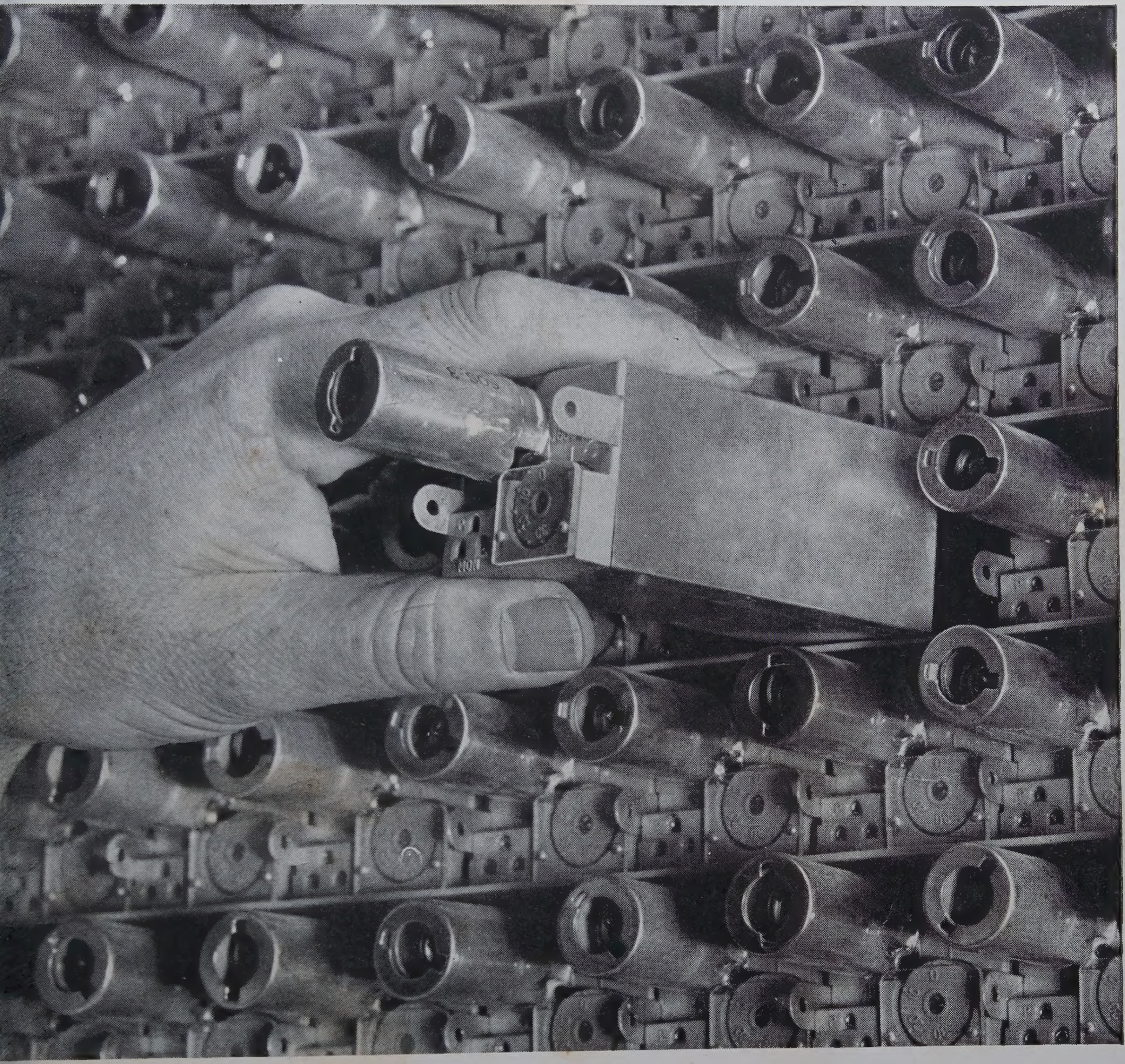

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